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DEPARTMENT OF ELECTRICAL ENGINEERING
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A FEASIBILITY STUDY OF A POCKET-SIZED GAS CHROMATOGRAPHIC AIR ANALYZER

by

Stephen C. Terry

John H. Jerman

July 1977

Final Report

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The feasibility of producing a pocket-sized air contaminant monitor based upon a miniature gas chromatograph and an integrated microcomputer has been demonstrated and a practical design for the instrument is presented. This pocket-sized instrument is intended to be used as a personal exposure monitor which is unobtrusively carried by an industrial worker throughout the day. The proposed instrument is fully self-contained in an 8 cm x 4 cm x 15 cm package weighing approximately 0.6 kg. It is built around a miniature integrated gas chromatograph (GC) consisting of a capillary column, a sample injection valve, and detector. A state-of-the-art integrated circuit microcomputer is included in the instrument to handle control and data processing functions. The proposed instrument will be capable of sampling the atmosphere automatically once a minute for eight hours, measuring the concentrations of up to 10 different vapors simultaneously to within 10% accuracy, calculating and storing the time-weighted-average and peak concentrations for each of the gases, measuring concentrations at the 10 ppm level, displaying any of the stored concentrations upon demand, and sounding an alarm when any concentration exceeds a predetermined value. The desirable features of this instrument — its small size, automatic operation, and ability to monitor multiple gases — should make it a useful analytical tool and of significant use in the fields of industrial hygiene and occupational safety.

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Disclaimer

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NIOSH Project Officer

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1. INTRODUCTION

Stanford University has conducted a one-year study of the feasibility of achieving a miniature gas analysis system based upon a recently developed "integrated" gas chromatograph fabricated on a silicon wafer. This study was completed under a National Institute for Occupational Safety and Health (NIOSH) contract, "A Pocket-Size Gas Chromatographic Analyzer for Chemical Contaminants in Air," No. 210-76-0140.

1.1 BACKGROUND AND PURPOSE

It is presently known that chronic exposure to a large number of the gases found in an industrial environment is potentially dangerous. It is also thought that there are levels of exposure which are low enough as to probably not be harmful. The Occupational Safety and Health Act of 1970 authorizes the Secretary of Health, Education, and Welfare to prescribe regulations requiring employers to measure, record, and make reports on the exposure of employees to these gases and substances which may endanger their safety or health. In order to prescribe such regulations, it is necessary and proper that the Secretary be able to provide or suggest to employers monitoring methods of suitable accuracy for making measurements of employee exposure.

Currently there are available several types of portable direct-reading instruments for the monitoring of single contaminants. These instruments can be used to monitor large work areas to obtain a record of a contaminant concentration in a general area and also to provide a warning if dangerously high concentrations of a contaminant are encountered in the area. The major problem with these instruments is that they do not measure an individual worker's exposure, thus ignoring the worker's mobility and the contaminant concentration fluctuations around a plant. The vast majority of existing instrumentation can only measure a single contaminant at a time and so one instrument must be obtained for each contaminant to be monitored.

Gas chromatography (GC) is an analytical technique widely employed in the chemical analysis of gases. Using the GC process, the constituents of a mixture of sample gases and vapors can be separated, identified, and measured. This technique can be used to detect and measure hundreds of different gases and vapors which might occur in air. Chromatography columns optimized for the detection of various industrial processing and output gases can be utilized in monitoring occupational health situations. Ideally, an industrial worker could be equipped with an unobtrusive, wearable, GC gas analysis system which would serve as a personal exposure monitor for several contaminant gases or vapors. At the present time, however, there are no suitably small and portable, commercially available GC and associated data analysis systems.

A recent development in the field of gas chromatography has been the application of integrated circuit (IC) processing technology to the miniaturization of the GC system. The extremely small geometries made possible by using IC photolithography and etching techniques drastically reduce the size and weight of the "integrated" GC column compared with conventional column structures. The small diameter of the integrated column makes it more efficient at separating vapors, and thus reduces the length of separator column needed to perform the separation and analysis. This reduction in length can cut analysis time from several minutes, as required by conventional columns, to a matter of seconds. Utilizing the same IC etching technology, miniature diaphragm valves for the sample gas injection system and a thermal conductivity detector are also integrated on the silicon wafer along with the GC column. Thus, it is now possible to fabricate a complete gas chromatography system on a single 5-cm diameter silicon wafer.

The development of large scale integration (LSI) technology has led to the emergence of integrated circuit memories, microprocessors, and digital calculators, all fabricated on single silicon chips. Utilizing this LSI technology, the data processing system for a GC·analysis system can be realized using several silicon chips. Combining the integrated data processing circuitry with the miniature integrated GC system should yield, for the first time, a truly pocket-sized, self-contained gas analysis system. Such an instrument would be ideal for a personal contaminant exposure monitor. This instrument would be capable of fitting in a worker's breast pocket, sampling and providing in a preprogrammed mode a real-time analysis of many different contaminants, providing an alarm function to warn against dangerous levels of each contaminant, and storing the information gathered to provide an estimate of the worker's time-weighted-average (TWA) exposure to each contaminant.

The purpose of this study was to analyze the technology currently available relative to the development of a pocket gas chromatograph designed to monitor a worker's exposure in occupational health situations, and to demonstrate the theoretical feasibility of such a system outlining necessary research needed to have it developed.

1.2 GC SYSTEM OVERVIEW

A completely self-contained gas chromatographic air analyzer, as shown in block diagram form in Figure 1, consists of a gas chromatograph for separating the contaminant vapors from air, and a microcomputer system for analyzing the GC output data and controlling the operation of the complete system. The chromatograph is capable of separating a mixture of gases into components and measuring the relative concentration of the parts. It does this by placing a brief pulse of sample gas at the head of a separating column. The pulse is blown down the column by the carrier gas flow. The column is coated with a lining material which can absorb and desorb the constituents of the sample mixture. Since a particular gas is stationary when absorbed in the column lining and moving when in the carrier gas, it will exit from the column at a slightly different time than another gas which is retained in the column lining

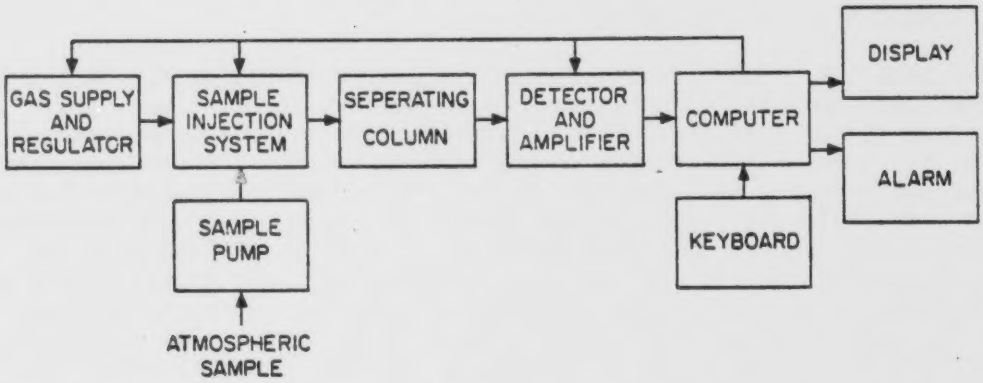

Figure 1. BLOCK DIAGRAM OF GAS ANALYZER SYSTEM.

for a different length of time. Since these characteristic retention times are different for a wide variety of different gases, a column can be very useful in separating a complicated mixture of gases.

In any gas analysis system it is also necessary to measure and record the amounts of gases found in the sample. In the miniature gas chromatograph this is done electronically. The output gas stream from the column is passed over a detector which measures a particular property of the gas, such as thermal conductivity, and measures the concentration of sample in the carrier. This signal is amplified and fed into a sophisticated microcomputer which analyzes the signal, determines the concentrations, and stores the data. If the concentration of any of the gases exceeds a certain threshold, the computer can sound an alarm which warns the user of a potentially dangerous situation. In addition, a keyboard and display are provided to allow the user to check the exposure information during the day.

There are a number of other parts of the system shown in Figure 1 which are necessary for proper operation of the gas chromatograph, including 1) the carrier gas supply, which provides a steady flow of carrier gas through the column, 2) the sample injection system, which places the brief pulse of sample gas in the carrier gas stream, and 3) the sample pump, which draws an atmospheric sample. These auxiliary systems are under the control of the microcomputer, which allows completely unattended operation of the entire instrument.

Such a system is only possible through the combination of the miniature gas chromatograph and a similarly miniaturized but still powerful computer system. It is capable of many functions not found in any other portable gas analysis system and is rather like having a laboratory instrument in the size of a pocket calculator.

1.3 ORGANIZATION OF THE REPORT

This feasibility report is based upon one year's investigation into all of the subsystems and components which comprise a pocket-sized, self-contained GC gas analyzer. These investigations include both experimental and theoretical studies of the component parts. Based upon these investigations, the next section of this report describes what we believe to be a feasible and practical realization of the pocket-sized instrument. The following section, entitled TECHNICAL EVALUATIONS, gives detailed descriptions of the design, fabrication technology, and present state of development of each of the major system components. As such, this section represents the main body of the feasibility study. Following that, the FUTURE DEVELOPMENT section summarizes the developmental effort that will have to be undertaken in each of the component areas to realize a first prototype of the proposed gas analyzer. The APPLICATIONS section briefly describes our view of how the proposed instrument will operate in the industrial environment, and what potential market exists for the device. Finally, the last section summarizes our results and conclusions.

2. PROPOSED IMPLEMENTATION OF A POCKET-SIZED GAS ANALYZER

Based upon our evaluation of the feasibility of the component parts in the miniature GC system, we have assembled what we believe to be a feasible and practical design for a fully self-contained pocket-sized gas analyzer. This design utilizes silicon "micromachining" techniques to fabricate the integrated gas chromatograph and advanced integrated circuits technology to realize the microcomputer, low power amplifiers, and the control and interface systems. Though many of the component systems have not yet been fabricated, we believe that their development lies within the framework of existing technology.

The following subsections very briefly describe the design of the proposed GC gas analyzer, its expected performance, some specific areas of development required to realize the device, and an estimated parts and labor cost breakdown for the manufacture of the instrument.

2.1 TECHNICAL DESCRIPTION OF PROPOSED SYSTEM

The miniature gas chromatograph, as shown in block diagram form in Figure 1, will be composed of the following sections:

1) Column
2) Injection system and sample pump
3) Detector
4) Amplifier and computer system
5) Keyboard and display
6) Carrier gas supply
7) Mechanical package and battery.

A brief description of the most likely realization of each of these sections is described below, while a more thorough description of the parts and the most promising alternatives is contained in the body of the report.

In the miniature gas chromatograph the column consists of a 1 meter long etched groove, about 20 μm (2×10^{-3}cm) deep by 200 μm wide, which is tightly coiled on a 5-cm diameter silicon wafer. A Pyrex glass cover is permanently bonded to the silicon wafer to convert this groove into a capillary column. The column is coated with a long chain hydrocarbon which acts as the lining material.

The injection system is used to introduce a small amount of atmosphere into the carrier gas stream as it enters the column. In the miniature system, a tiny diaphragm valve is fabricated on the same silicon wafer as the column. This miniature valve features a replaceable diaphragm and is activated by a small solenoid to introduce reproducible

1-nl($1 \times 10^{-6} cm^3$) volumes of pressurized sample gas into the carrier gas at the head of the separating column. The atmospheric sample is pressurized to approximately two atmospheres by a 0.25-cm^3 syringe pump which is driven by a miniature mechanical servo.

The detector consists of 250-μm diameter thermistor bead which is mounted on a removable detector assembly. This detector assembly is a small portion of another silicon wafer and is fastened directly to the silicon wafer which contains the separating column to minimize dead volume. The entire internal gas volume of the miniaturized GC, including injector, column, and detector, is less than 10 μl. This small volume is necessary for portability and high speed operation.

The detector amplifier is a relatively common operational amplifier, the Fairchild μA725, which feeds information to the computing system. The main part of the computer system is the Intel 8748 microcomputer chip. This single part contains numerical processing, control, timing, program memory, data memory, and input/output circuitry on a single silicon chip. The 8748 is the most sophisticated miniaturized computer yet built, and complements the integrated gas chromatograph. Some additional electronic CMOS*memory is used to store the values of the peak, time weighted average, and most recent impurity gas concentrations as calculated by the microcomputer.

A numerical display and simplified keyboard are included to allow the user to retrieve concentration data from the computer's memory. In addition, an audible alarm is provided to warn the user of gas concentrations above the applicable standards.

The carrier gas supply consists of a 10-cm^3 helium gas cylinder, which contains enough carrier gas to provide the nominal 1 μl/sec carrier gas flow for many days. There is an integrated pressure regulator consisting of another modified diaphragm valve, a silicon pressure sensor, and a surge cavity to provide a constant pressure gas supply for the column.

The package includes a single 6-volt rechargeable battery of sufficient size to power the unit for an entire 8-hour day. All components listed above are fitted in a package similar in size to many early pocket calculators.

It should be emphasized that this is a preliminary product description, and only certain portions of the finished instrument have been tested. While certain sections will undoubtedly be redesigned, this summary represents the most likely final design.

2.2 EXPECTED PERFORMANCE

The fully self-contained portable gas analyzer should be capable of unattended automatic operation for periods of up to eight hours per battery charge. After an eight-hour day's use, a ten-hour (overnight) recharge will be necessary for continued operation. It is expected that the useful lifetime of the nickel-cadmium battery in the instrument will

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* See Glossary

be from 300 to 1,000 such charge-discharge cycles. The helium carrier gas supply, contained in a disposable 10-cm^3 gas cartridge should be capable of providing approximately eighty hours of carrier gas flow to the GC system.

The ultimate detectivity of the instrument, expressed as a parts-per-million (ppm) concentration of contaminant vapor in air, is projected to fall within the range of 10 to 50 ppm. This detectivity is limited by the response of the thermal conductivity detector, amplifier noise, and the peak broadening which occurs in the capillary column and the detector. With further development of the detector and the amplifier system, the minimum detectable concentration at the detector should be about 1 ppm, resulting in a system detectivity of about 10 ppm for slightly-retained compounds, up to 50 ppm for vapors retained as long as 15 seconds.

The resolution of the GC system, its ability to separate and identify very similar compounds, is in question at this point. As in any GC system, proper choice of the column lining and operating conditions are of paramount importance in optimizing the analysis of a specific set of compounds. To date, only a limited number of linings and operating conditions have been evaluated, and column performance appears to have been limited by the detector rather than by the lining. Again, with improved detector performance, the GC system should be capable of performing moderately difficult separations of ten compounds. However, final determination of the instrument's ability to separate and measure compounds of interest can only be made after the column lining and detector system have been further developed.

2.3 DEVELOPMENT EFFORT

A significant amount of developmental effort must be invested in this device before it is ready for commercialization and is available to industry as an off-the-shelf item. The next logical step in the evolution is the development of a hand held prototype model. Achievement of the desired performance goals (8-hour operation, 10-ppm detectivity, and resolution and measurement of 10 gases) will require improvements in the present column linings, valves, and detector. The miniature valves must be further reduced in volume, and the solenoid actuators made more efficient. The thermal conductivity detector which is presently integrated on the silicon wafer with the capillary column must be reduced in volume and redesigned to be removable and replaceable. In addition, the sophisticated, low power electronics system for the instrument will have to be designed and fabricated using custom integrated circuit components and a CMOS microcomputer, which although not yet available, is expected to be made available during the development period. To realize all of the developments and improvements in the system will require the use of high technology silicon etching, integrated circuit fabrication, and hybrid electronics packaging. With the availability of these technologies and facilities, it is estimated that about six man-year's worth of effort will be required to build a prototype version of the miniature GC gas analyzer.

2.4 DIRECT COST

To some degree, the ultimate utility of the eventual pocket-sized system will be dependent on the purchase price of the individual units to the user. In an effort to predict the final retail cost, a preliminary direct cost and direct labor analysis was performed and is shown in Table 1. The component prices are roughly those at the 1000 unit level and thus represent the minimum attainable cost for the maximum probable production levels possible for the miniaturized gas chromatograph in the near future. Small unit quantities of a majority of the components are about twice as expensive as the 1000 unit level, so the total small-unit direct cost is about $400. The number of hours of direct labor is somewhat dependent upon the sophistication of production methods employed. These figures were derived on the assumption that no production oriented processing equipment was available, which is reasonable yet conservative.

There is, of course, a great deal of uncertainty in the various figures due to a lack of exact knowledge of the final configuration of the instrument. Construction of a prototype would substantially reduce this uncertainty, but the retail price will most likely be between $850 and $2000.

TABLE I

DIRECT COST BREAKDOWN AT 1000 UNIT LEVEL

Section Components	Price ($)	Time (hrs)
Column and Tubes		
Silicon wafer - double polished 50% yield	10.00	
Masks	2.50	
Chemicals	2.00	
Processing		5.0
Glass/silicon bonding	4.00	.5
Tube mounting block	5.00	
Tubes and fittings	15.00	.5
Column linings	1.00	.5
	39.00	6.5

Table I continued

Valves		
2 solenoids	20.00	
2 diaphragms 50% yield	2.00	
Assembly, alignment		.5
	22.00	.5
Detector		
Thermistor 70% yield	5.00	
Replaceable detector cavity	5.00	.5
Assembly time		1.0
	10.00	1.5
Gas Supply and Pressure Regulator		
Gas cylinder	5.00	
Cylinder holder & block	5.00	
Pressure sensor	7.50	
Surge cavity	.50	
Assembly		1.0
	18.00	1.0
Injection System		
Servo	10.00	
Pump	5.00	
Check valve	1.00	
Pressure sensor	.50	
Filter	2.00	
Assembly		1.0
	25.50	1.0

Table I continued

Electronics		
Microprocessor Intel 8748	10.00	
I/O drivers	3.50	
1K RAM and latch	4.00	
A/D converter 12 bit	7.50	
Detector amplifier	4.00	
Analog multiplexer	1.00	
Comparator	1.00	
Hybrid package and circuit board	15.00	
Assembly	5.00	3.0
Display drivers	1.00	
Keyboard	2.50	
Alarm	2.50	
Misc. components	3.00	
	63.00	3.0
Mechanical		
Case and hardware	10.00	1.5
Batteries and holder	12.00	
	22.00	1.5
Accessories		
Instruction book	3.00	
Carrying case	5.00	
Packing carton	2.50	
Spare filters	2.50	
Packaging		.5
	13.00	.5
Final test and calibration		1.5
Grand total	212.50	17.0

3. TECHNICAL EVALUATION OF SYSTEM COMPONENTS

This section is a technical evaluation of the various subsystems and components which comprise the pocket-size GC gas analyzer. The feasibility of realizing each of the components with both size and performance characteristics appropriate for the instrument is evaluated. The major subsystems which were investigated are: 1) capillary columns and column linings, 2) sample valves and injection systems, 3) detectors, 4) detector amplifiers, 5) microprocessor system, 6) carrier gas supply, 7) battery power supply, and 8) the mechanical package.

Conclusions as to the feasibility of these subsystems and components are based upon experimental work in the areas of column linings, miniature valves, thermal conductivity detectors, and microcomputer systems, and on purely theoretical evaluations of alternate detector systems, amplifiers, pressure regulators, batteries and expected column performance.

Since the sensitivity and resolution of the GC systems will be ultimately determined by the performance of the detector and column lining, the feasibility of several alternative implementations in these areas is discussed, while for most of the other system components, only the most feasible approach is described.

3.1 MINIATURE CAPILLARY COLUMNS

The miniature capillary columns previously developed at Stanford University [1] are the heart of the miniature GC system and have demonstrated the feasibility of integrating a complete GC system on a wafer of silicon. The following subsections describe the fabrication of the capillary columns, the column lining techniques which we have investigated, the GC separations which have been achieved to date and an evaluation of the achieved and predicted performance of the integrated gas chromatograph.

3.1.1 Capillary Column Fabrication

The integrated capillary column is formed by etching a long spiral groove into the surface of a silicon wafer and then hermetically sealing the wafer to a Pyrex glass cover plate (shown in Figure 2). The cross section of the resulting gas channel is roughly rectangular, with a width of 200 μm and a depth of 20 μm. Columns up to 3 meters in length have been fabricated in this manner. Holes etched through the wafer at the ends of the gas channel serve as entrance and exit ports for the carrier gas.

Fabrication of the column structure proceeds in a sequence of photolithography and etch steps very similar to the photolithography and diffusion steps of standard IC device processing. The starting material is a 5-cm diameter silicon wafer of (100) orientation. A layer of silicon dioxide

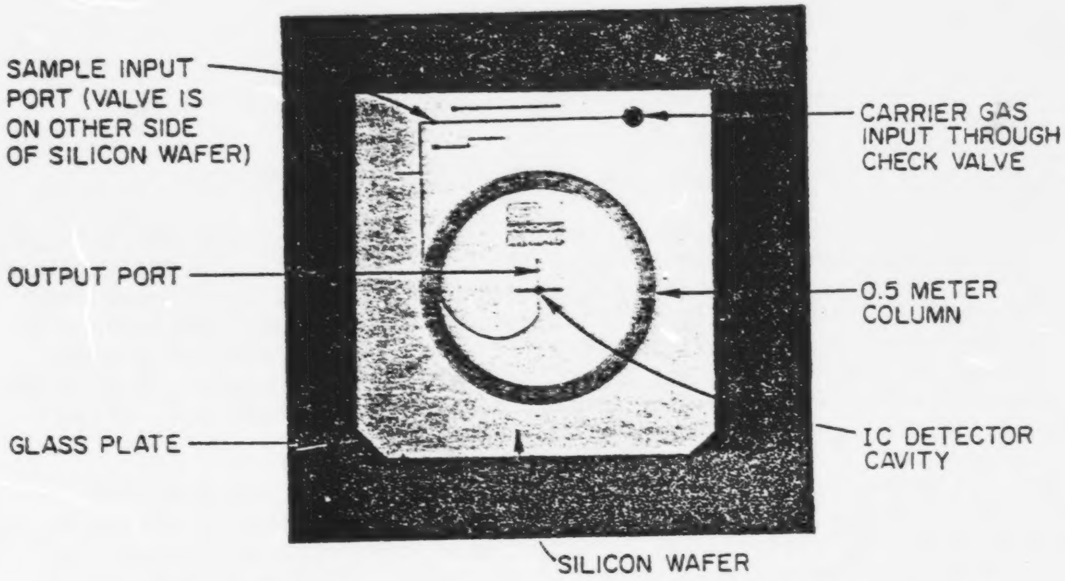

SAMPLE INPUT PORT (VALVE IS ON OTHER SIDE OF SILICON WAFER)
OUTPUT PORT
GLASS PLATE
CARRIER GAS INPUT THROUGH CHECK VALVE
0.5 METER COLUMN
IC DETECTOR CAVITY
SILICON WAFER

Figure 2. PHOTOGRAPH OF MINIATURE GC SYSTEM. The etched silicon wafer is viewed through the 5-cm square Pyrex glass cover plate.

(SiO_2) approximately one μm thick is thermally grown on the wafer to serve as an etch mask in the silicon etching step. The spiral pattern for the groove is photographically reproduced on a glass plate to serve as a photolithography "mask." Using a standard photoresist and photolithography process, the spiral pattern is then defined in the SiO_2 on the front side of the silicon wafer; the oxide is removed where the groove is to be formed, exposing the silicon surface. The wafer is then placed in a silicon etching solution where the spiral pattern, unprotected by oxide, is etched into the silicon.

Several groove cross-sectional profiles are available, depending on the silicon etchant used and the conditions under which the etch is performed. An anisotropic etchant such as potassium hydroxide (KOH) results in a V-groove profile in (100)-oriented silicon, as is shown in Figure 3a, and in a vertical wall profile in (110)-oriented silicon (Figure 3b). A mixture of hydrofluoric and nitric acids can be used as an isotropic silicon etchant to produce the grooves shown in Figure 3c. This HF-nitric etch is utilized in forming the miniature capillary column since it produces approximately rectangular grooves oriented in any direction on the wafer.

After the capillary groove and gas exit holes have been etched, the silicon wafer is cleaned and stripped of all oxide, and a 5-cm square Pyrex cover plate is anodically bonded to the wafer. The anodic bonding process [2] is a relatively low temperature technique with which Pyrex glass can be bonded to silicon without the use of any bonding agent or other filler material. The silicon and Pyrex wafers are held together and heated to approximately 400°C. A 600-volt potential is then applied between the

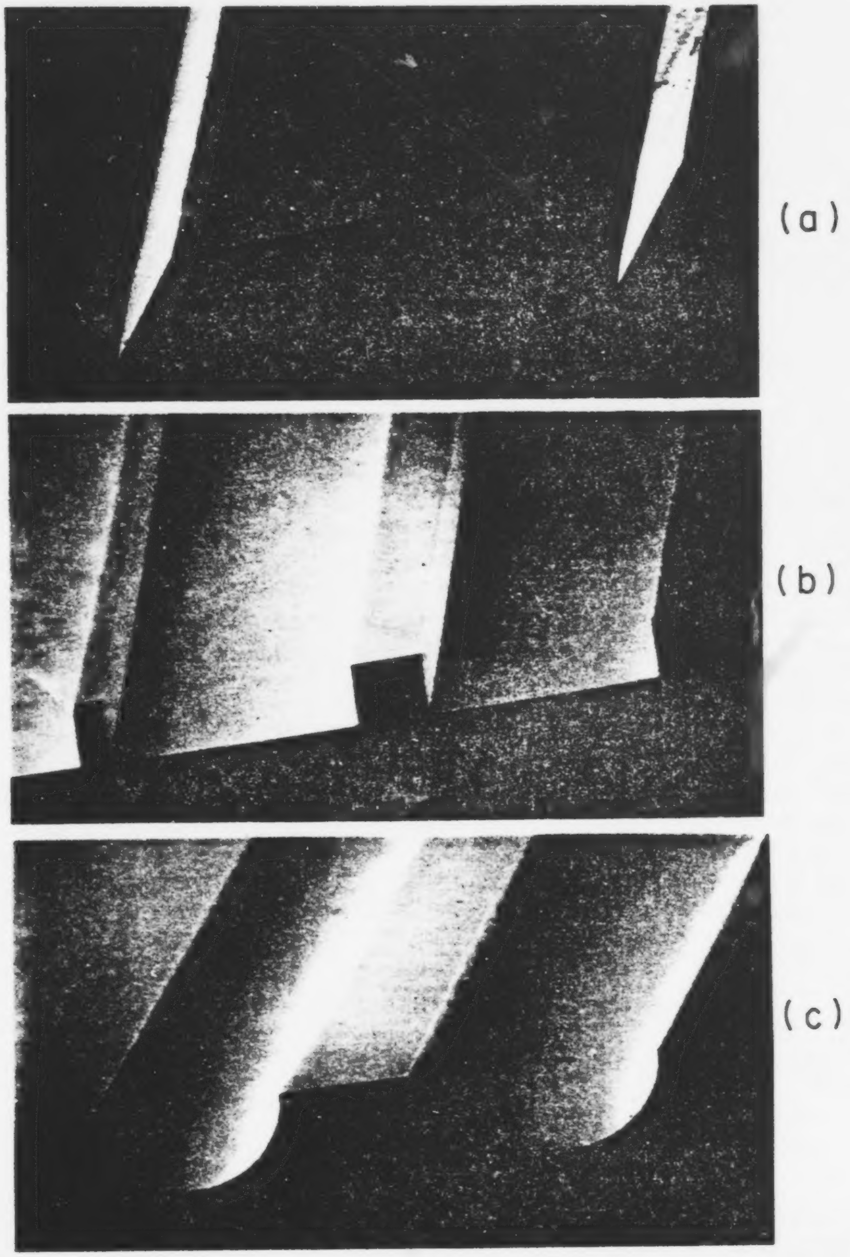


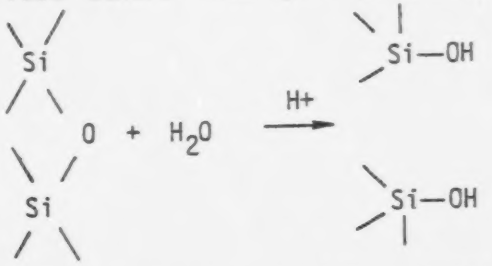
Figure 3. SEM PHOTOGRAPHS OF GROOVES ETCHED IN SILICON, APPROX. 500X. (a) KOH etch in (100) silicon, (b) KOH in (110) silicon, and (c) $HF-HNO_3$ etch.

glass and silicon, and the resulting electrostatic force pulls the wafers into intimate contact. At the elevated temperature and in the presence of high electric fields, bonding is almost instantaneous. The resulting seal between the glass and silicon is irreversible and hermetic, thus forming the spiral groove into an enclosed capillary tube. At least 40 integrated capillary columns have been fabricated to date using the process described above. These columns have been of various depths and widths and have ranged from 1 cm to 3 meters in length. The fabrication process appears to be well controlled and reproducible, and it results in an approximate 80% yield of good columns.

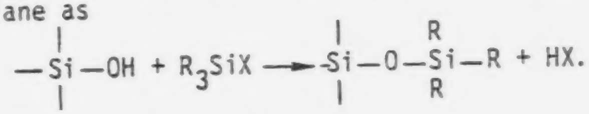
3.1.2 Column Linings

The previous work on the miniature capillary columns [1] indicated that there were severe problems associated with achieving an ideally uniform and thin layer of stationary phase on the column walls. The surface tension of the liquid phase is sufficient to cause beading and puddling of the liquid even when a wetting agent was included in the lining liquid. This has long been a problem associated with conventional capillary columns, but the extremely smooth column walls and nonconstant radius of curvature of the capillary cross section serve to magnify the problem in the integrated capillary column. It is generally agreed that some sort of surface modification is necessary either to give the lining liquid surface niches in which to reside or to make the surface more wettable by the lining. Since the first approach does not appear to be compatible with the column fabrication process, a two-pronged effort was launched to investigate the use of organosilanes as chemically-bonded wetting agents and/or as chemically-bonded liquid phases themselves.

The construction of the integrated capillary column is such that the capillary bottom and side walls are silicon while the top plate is glass; however, the silicon surface is coated with a layer of silicon dioxide (SiO_2) several tens of Angstroms thick which is grown during the anodic bonding process. The SiO_2 and glass surfaces are covered with a high density of silyl ether and hydroxyl groups. Treatment of these surfaces with an aqueous solution of a strong acid (e.g. concentrated HCl) converts many of the surface ethers into hydroxyl groups.



These surface hydroxyl groups will react with organosilane compounds of the form $RSiX_3$ or R_3SiX (where R is an alkyl group and X is either a chloride or an alkoxide group) to form a Si-O-Si linkage between the silicon and the silane as

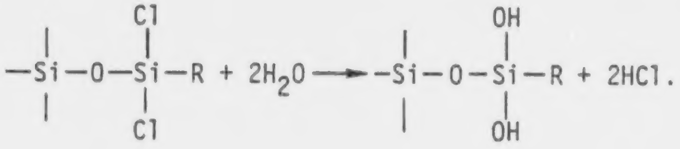


$$-\overset{|}{\underset{|}{Si}}-OH + R_3SiX \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{R}{\underset{R}{Si}}-R + HX.$$

We have employed this chemistry to form bonded liquid phases and to attach wetting agents to the column surfaces. A brief description of the compounds and processes that we tried follows.

Trichloroeicosylsilane ($Cl_3Si(CH_2)_{19}CH_3$)--

The column which was to be lined was first washed with concentrated HCl, then filled with a 5% solution of the silane in benzene and allowed to sit for several hours at room temperature. It was then blown dry, washed with xylene and then methanol, and blown dry again. The purpose of using the trichloroeicosylsilane compound was two-fold. We wished to examine it as a permanently bonded stationary phase and as a wetting agent for nonpolar liquid phases. Columns treated with this substance retained test gases (acetone, pentane, ethanol) very slightly. The order of retention, however, was not what would be expected of a totally nonpolar column i.e. ethanol was retained longer than pentane. This was probably due to free hydroxyl groups generated upon hydrolysis of unreacted Si-Cl groups:



$$-\overset{|}{\underset{|}{Si}}-O-\overset{Cl}{\underset{Cl}{Si}}-R + 2H_2O \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{OH}{\underset{OH}{Si}}-R + 2HCl.$$

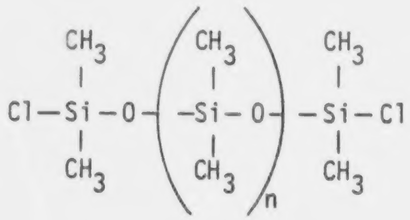
The silane compound did prove satisfactory as a nonpolar wetting agent.

Trimethylchlorosilane $(CH_3)_3SiCl$--

Reaction was carried out by forcing the undiluted silane through the column for about one hour at 70°C. The capillary was then washed out with water and methanol and lined by passing a plug of nonpolar stationary phase (Apiezon L in heptane solution) through the column. The silane compound proved satisfactory as a wetting agent for the nonpolar linings.

Dimethylsiloxyl polymer--

The polymer was prepared by allowing dimethyldichlorosilane (DMDCS) vapors and water vapor to diffuse together in a closed vessel over a period of several days. The resulting polymer was extracted into benzene, dried, and treated with more DMDCS. The excess DMDCS was removed under vacuum leaving the polymer



$$Cl-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left(-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right)_n-\overset{CH_3}{\underset{CH_3}{Si}}-Cl$$

This polymer, intended to be used directly as the liquid phase, was chemically bonded to the column walls by forcing it through a column for one hour while heated to 70°C, and then washing the column successively with dichloromethane, water, and methanol. The treated column retained the test vapors slightly, in the order expected of a polysiloxyl ether.

γ-aminopropyltrimethoxy silane $NH_2(CH_2)_3Si(OCH_3)_3$--
The γ-aminopropyltrimethoxy silane was dissolved in xylene (5% by volume) and flushed through the column while heated to 70°C. It was then flushed out and the column was lined with a solution of Carbowax 400 in dichloromethane. This resulted in a uniformly distributed layer of the very polar Carbowax 400 stationary phase.

Concentrated HCl Surface Preparation--
It was discovered that a column treated with concentrated HCl for several hours could also be directly lined with Carbowax 400. Though this method tended to destroy the integrated TC detector, it was used to replace the more complicated aminosilane lining procedure.

All of the lining procedures described above appeared to give uniformly distributed layers of stationary phase in the column. Under examination with a high power light microscope, none of the beading and puddling of the lining which had previously been a problem was observed. Even very thick linings of Carbowax 400 (20% in dichloromethane) showed no tendency to bead up and blow out of the column. Thus, from the standpoint of being able to introduce uniformly appearing linings into the columns, we have succeeded in realized lining techniques for both polar and nonpolar stationary phases.

3.1.3 GC Separations

In an attempt to get good quantitative data on the quality of the column linings, actual GC separations were performed with several integrated GC systems and column linings. The polar lining (Carbowax 400), nonpolar lining (Apiezon L), and bonded dimethylsiloxyl polymer lining were evaluated on 50-cm long, 20-μm deep capillary columns.

Due to factors which are unrelated to the column linings, the data which has been obtained thus far has been only of qualitative value in evaluating column lining performance. The problem appears to be associated with both the volume and the geometry of the integrated TC detector currently being used. Consideration of the air peak, which should be totally independent of the column lining, reveals that gas mixing processes in the relatively large detector cavity (100-nl volume) are broadening the air peak by up to a factor of 100 over the broadening which can be explained by sample gas phase diffusion and pressure effects. This is supported by the observed fact that the air peak width is directly proportional to its retention time instead of proportional to the retention time to the three-halves power which would be expected if diffusion processes were accounting for the peak spreading. If the unabsorbed air peak is being grossly broadened by the detector, the sample peaks can be no narrower, and will thus falsely indicate very poor column performance. The detector geometry is another factor affecting the observed peak widths. In the detector's present configuration (see Figure 2), the channels for the thermistor's leads can collect large amounts of the liquid phase during the column lining process. This large volume of lining at the detector tends to absorb and desorb vapor very slowly, thus leading to very broad vapor peaks independent of the lining on the rest of the column. Such an effect is supported by the gross vapor peak broadening observed when only the detector is lined with stationary phase. For these reasons any serious attempt at quantitative evaluation of column linings and lining techniques at this time is fruitless. There are, however, a number of qualitative observations about the present column linings that can be made and which are encouraging.

Nonpolar Stationary Phase (Apiezon L)--

Figure 4 shows the output chromatographs obtained on columns lined with 5% and 0.5% Apiezon L. As expected, the column with the thicker lining (5% Apiezon L) retained heptane longer than the 0.5% column. Also, the heptane peak from the 0.5% column shows significant tailing, indicating that the lining is being overloaded with sample. Golay plots of theoretical plate height (HETP) versus flow rate were made for the two columns. The plot of heptane on 5% Apiezon (Figure 5) resembles a normal Golay plot, while the plot for 0.5% Apiezon was wildly scattered and was totally useless. The separation corresponding to the minimum HETP of Figure 5 is shown in Figure 4a.

However, as mentioned in the beginning of this section, any attempts to determine column efficiency are meaningless since the detector is significantly broadening the peaks. For example, the air peak in Figure 4 is roughly 500 msec wide at its base, whereas it should only be 40 msec in width.

Polar Stationary Phase (Carbowax 400)--

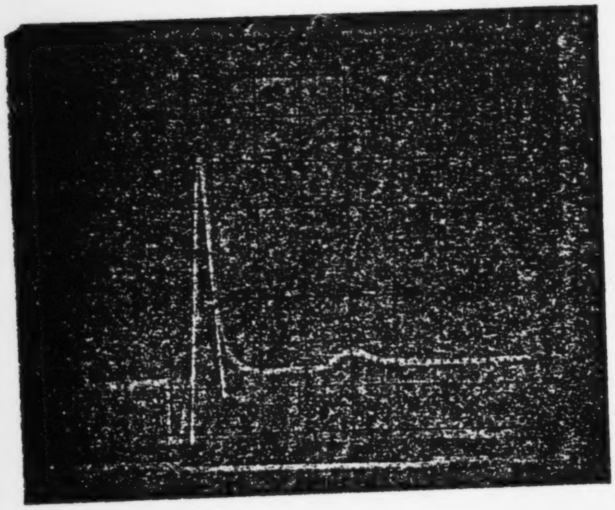
A separation of acetone from air on a 20% Carbowax 400 lining is shown in Figure 6. Once again the peaks are grossly broadened by the detector; however, complete separation is achieved in only 6 seconds. The tailing of the acetone peak is in part due to the thick lining in the detector, and partly due to hydrogen bonding between the acetone and Carbowax which occurs when the column is operated at room temperature. A Golay plot of HETP versus flow for this column has approximately the right shape for a normal Golay plot; but once again, the numbers obtained with such an analysis are meaningless due to detector problems.

Bonded Polymer Linings--

The output chromatogram showing the retention of heptane on a 50-cm column lined with dimethylsiloxyl polymer is shown in Figure 7. The chromatogram is traced on an oscilloscope with a sweep speed of 200 milliseconds per division. The heptane (large positive peak) is only slightly retained from the helium in the sample (negative peak); and in fact, if heptane had been mixed with air instead of helium in the sample gas, the heptane peak would have been completely masked by the large, almost coincident, air peak. There are two points to be noticed in this chromatograph:

1) There is a slight retention of the heptane with respect to the helium peak (approximately 200 msec), and

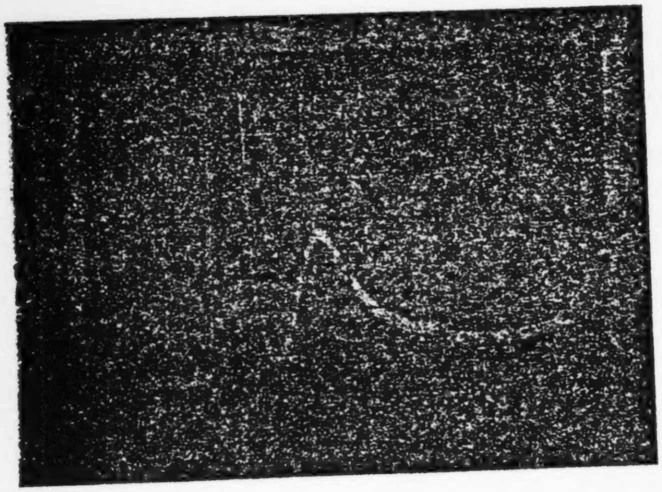
2) The heptane peak is badly distorted from its ideal gaussian shape. These two observations indicate that there was indeed a lining in the column which was accounting for the heptane retention, however it was being overloaded by the size of the heptane sample. The retention is gratifying to observe



Vertical scale
0.2 V/div

Horizontal scale
2 sec/div

(a) Separation of Helium, Acetone, and heptane. Column lining - 5% Apiezon L; Helium carrier gas; sample 2.2% heptane, 11% Acetone, 86.8% Helium



Vertical scale
0.1 V/div

Horizontal scale
0.5 sec/div

(b) Separation of air and heptane. Column lining -- 0.5% Apiezon L; Helium carrier; sample 2.2% heptane, 97.8% air.

Figure 4. CHROMATOGRAMS OBTAINED FROM MINIATURE GC USING APIEZON L LINING.

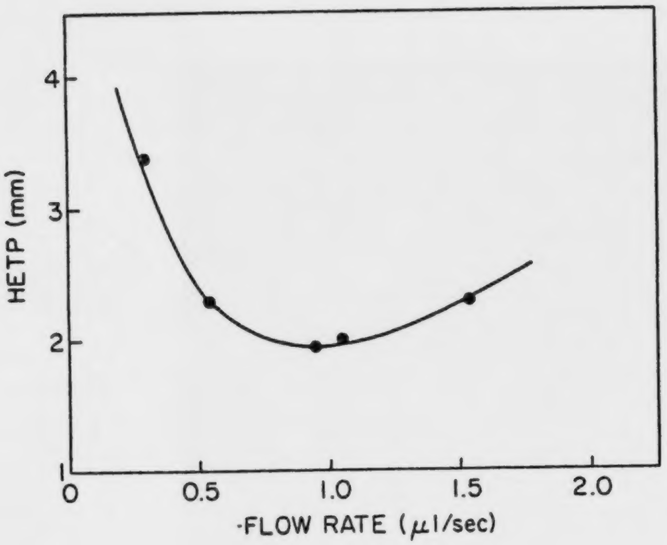
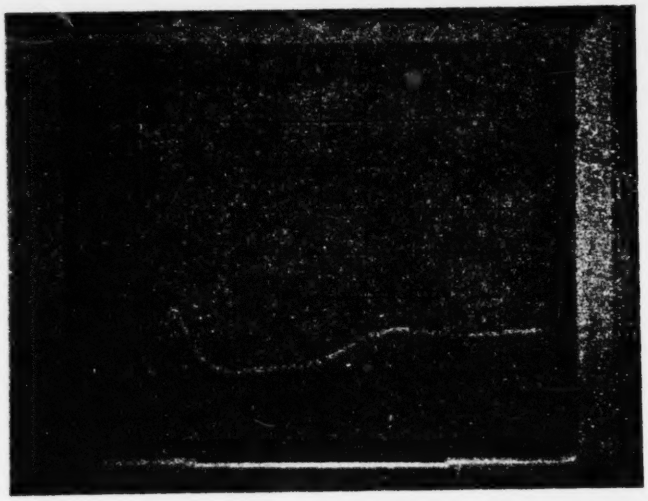


Figure 5. PLATE HEIGHT VERSUS FLOW RATE OBTAINED ON A MINIATURE COLUMN (heptane on 5% Apiezon L).

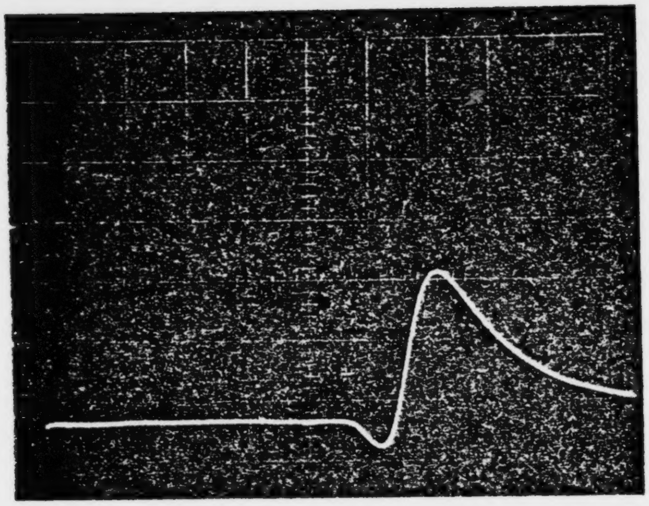


Vertical scale
0.2 V/div

Horizontal scale
2 sec/div

Separation of air, Acetone, Ethanol. Column lining 20% Carbowax 400; sample 2.8% Ethanol, 11% Acetone, 86.2% air.

Figure 6. CHROMATOGRAM OBTAINED FROM MINIATURE GC SYSTEM USING CARBOWAX 400 LINING.



Vertical scale
0.1 V/div

Horizontal scale
200 msec/div

Separation of helium and heptane. Column lining - dimethylsiloxyl polymer; sample 2.2% heptane, 97.8% helium.

Figure 7. CHROMATOGRAM OBTAINED FROM MINIATURE GC WITH BONDED POLYMER LINING.

since it indicates that the extremely thin column lining (less than 100 Å in thickness) is actually performing as a stationary phase, and if the sample injections could be reduced so as not to overload the column, it might prove to be sufficient for adequate separations. However, since of all the gases of interest heptane is one of the most highly retained by this lining, and since it will be difficult to greatly reduce the sample size while still being able to detect the output peaks, it is doubtful that the bonded polymer stationary phases will ever prove to be useful in the integrated capillary columns.

3.1.4 Evaluation of GC Performance

The performance of the complete GC system can be evaluated from the separations shown in Figures 4, 6, and 7. Since the peak spreading caused by the detector is included in the complete system performance, it does not have to be separated from the spreading caused by other sources, and hence does not preclude quantitative evaluation of the system as it did in the column lining investigation. At present the detector is significantly limiting the performance of the GC system; but since this problem should be overcome in the future, it is best to divide this discussion into segments of current, expected, and required performance.

Current Performance--
Typical separations obtained with the integrated capillary columns are shown in Figure 4 for acetone and heptane on Apiezon L and Figure 6 for acetone and ethanol on Carbowax 400. These separations can be evaluated for various measures of system performance, namely HETP, partition ratio k, number of plates (N) in the column, and separation factor S. These parameters, defined in Appendix 1, are used to relate the peak spreading, retention times, and ability of a column to separate two adjacent peaks. The values of these parameters as determined from Figures 4 and 6 are presented in Table 2. The values of partition ratio k (the retention of a vapor peak divided by the retention of the air peak) are in the right range (2-10) for capillary columns, indicating that there is sufficient stationary phase in the columns to substantially retain the peaks. The very small number of theoretical plates in the column and the low separation factor indicate the poor performance of the GC, since both of these parameters should ideally be in the thousands. Also, to be comparable to standard capillary columns, the HETP should be no larger than 1 mm.

Table 2. Column parameters obtained with two integrated GC systems.

Column Lining	Output Peak	Partition Ratio, k	HETP (mm)	No. of Plates N	Separation Factor, S
Apiezon L	Acetone	1.33	1.6	306	100
Apiezon L	Heptane	2.9	1.7	300	165
Carbowax 400	Acetone	2	12.5	40	18
Carbowax 400	Ethanol	8.1	9.4	53	42

In all fairness to the column, it must again be stated that a major amount of the peak broadening is believed to be caused by the detector volume and the collection of stationary phase in it. It is clear that if these problems are not solved, the integrated GC will not achieve much better performance than is evidenced in Figures 4 and 6.

Expected Performance--
There are three means whereby the performance of the miniature integrated GC can be improved: 1) correct the volume and lining problem associated with the detector, 2) increase the column length, and 3) optimize the column depth and the lining for the separations being performed. Improving the detector will be approached by going to the removable detector design which is described in the detector section of this report. The reduced volume of this detector and the fact that the detector itself will not be lined with stationary phase should virtually eliminate the gross peak spreading which is now occurring. The air peak width should be reduced by a factor of 10 to 100, with the result that better resolution of slightly retained peaks will be possible.

Increasing the column length from 0.5 m to 3 m is also possible with the integrated GC. Since the separation factor S is directly proportional to column length (see Appendix 1), this would result in a six-fold increase in the separating power of the GC. However, the optimum length of the column may be shorter than 3 meters, since increased length results in higher gas pressures and longer analysis times. The final length will have to be determined after the column linings can truly be evaluated and the desired separations are set forth.

The performance of the GC column can be greatly influenced by the depth of the capillary groove and the thickness of the stationary phase layer on the column walls. Figure 8, reproduced from reference [1], indicates how the plate height (HETP) and separation factor vary as a function of the column depth. Using typical column parameter values listed in the figure, it can be seen that for the Z_0 = 10 μm column depths currently being used, we should be observing plate heights of 0.3 mm and separation factors of 2000 instead of those listed in Table 2. Further optimization of the carrier gas flow rate will yield a slightly higher separation factor than indicated in Figure 8, however, even attainment of a separation factor of 2000 would represent more than an order of magnitude improvement over current results.

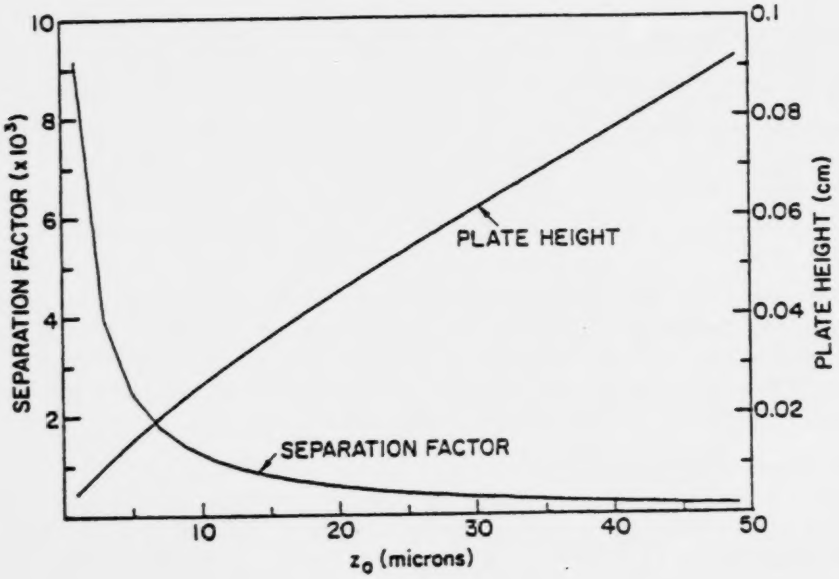


Figure 8. SEPARATION FACTOR AND PLATE HEIGHT AS FUNCTIONS OF COLUMN DEPTH ($2Z_0$). Theoretical calculations are based upon a rectangular column 100 cm long, lining thickness 0.5 μm, carrier flow 100 cm/sec, and partition coefficient K = 100.

Required Performance--
For the integrated GC to be effective as an analytical instrument and feasible as a portable gas analyzer, it must be capable of separating the gases of interest from themselves and from air. Some of the gases and vapors of interest for the personal air contaminant monitor are listed in Table 3. The choice of a liquid phase to be used to separate these compounds is determined primarily by the separating power of the column and exactly which compounds are expected to be found together. Because of the relative diversity of the compounds, it is not obvious what type of liquid phase might be best suited. The compounds generally (though not all) have some degree of polarity, thus suggesting that a somewhat polar liquid phase might be in order. In the final analysis, the proper choice of liquid phase will have to be made based upon how efficient the integrated GC can be made, and what separation factors can be achieved.

Table 3. Gases of interest.

Contaminant	Fed. OSHA Standard (ppm)
Pentane	500
Hexane	100
Cyclohexane	300
Ethyl Acetate	400
n-Amyl Acetate	100
Methanol	200
Acetone	1000
Methyl Ethyl Ketone	200
Ethyl Ether	400
Ethylene Dibromide	20
Methyl Chloride	100
Trichloroethylene	100
Ethylene Dichloride (1,2-Dichloroethane)	50
Toluene	100

In the meantime, it is instructive to look at the gases of interest and the stationary phases which have already been used, and to determine the separation factors needed to achieve complete separation of all the compounds listed. As detailed in Appendix 1, the separation factor required for complete separation of two vapors with very similar retention characteristics can be determined from the knowledge of their relative retentions on the stationary phase of interest

$$S = 32\left(\frac{V_{R_2}}{V_{R_2} - V_{R_1}}\right)^2.$$

Specific retention volumes can be found in the literature [3,4] for most of the compounds on both Apiezon L and Carbowax 400. From the high temperature data points given, we can roughly extrapolate back to get the retention volumes at room temperature (25°C) where the miniature columns will be operating. Table 4 lists this data along with the calculated separation factor required to separate each pair of compounds.

On the Carbowax stationary phase, the most difficult separations are methylene chloride from ethyl acetate requiring a separation factor of S = 2397 and methylene chloride from methyl ethyl ketone requiring S = 11,465. The latter separation on Apiezon L stationary phase would require S = 109, illustrating the importance of proper selection of stationary phase for separation of specific sets of compounds.

The values of specific retention volume and separation factors given in Table 4 cannot be taken as exact, due to the gross extrapolation required to get from published data at 120°C to the column temperature of 25°C. They do, however, give a good indication of the degree of difficulty which will be encountered in performing many of the separations. Provided that gross peak tailing due to low temperature operation is not a limiting factor, Table 4 indicates that with either column lining, a separation factor of 500 would be sufficient to resolve all but four pairs of compounds. Such a separation factor should be readily achievable by the miniature columns since it is well below the theoretical value shown in Figure 8, and it represents only a factor of 5 improvement in the performance of the Apiezon L column currently in use.

We are optimistic that the performance of the integrated GC system can be improved sufficiently to realize separation factors in the range of 500 to 1000 and thus achieve complete or at least adequate separations of most of the compounds of interest.

3.2 DETECTORS

After the sample gases have been separated, the individual peaks must be detected as they evolve from the column. Even if the column is capable of performing perfect separations, the ultimate detectivity of a GC system is usually dependent upon the performance of the detector.

In the miniature GC systems constructed to date, a thermal conductivity detector in the form of a miniature thermistor bead has been used because of its simplicity of construction and operation.

A review of the operation, construction, and performance of thermal conductivity detectors is given below, followed by a review of other types of detectors which offer the possibility of a more sensitive system.

TABLE 4: RETENTION & SEPARATION FACTOR DATA

Compound Retentions on Carbowax 400		Separation Factor
Compound	Retention Volume *@ 25°C	Necessary to just separate peaks of pairs of compounds
Pentane	7	
		128
Hexane	14	
		2,048
Ethyl Ether	16	
		51
Cyclohexane	77	
		170
Acetone	136	
		213
Ethyl Acetate	222	
		2,397
Methylene Chloride	251	
		11,465
Methyl Ethyl Ketone	265	
		175
Methanol	463	
		843
Toluene	575	
		96
n-Amyl Acetate	1,352	

Compound Retentions on Apiezon L		Separation Factor
Compound	Retention Volume *@ 25°C	Necessary to just separate peaks of pairs of compounds
Methanol	8.3	
		96
Acetone	19.6	
		266
Methylene Chloride	30	
		117
Ethyl Acetate	63.0	
		21,966
Methyl Ethyl Ketone	65.5	
		219
Hexane	106	
		52
Toluene	493	
		108
n-Amyl Acetate	1080	

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* The specific retention volume @ 25°C was determined by extrapolation from published data [3,4] at 120°C, 100°C, and 80°C using the exponential temperature dependence of the partition coefficient $K \alpha \exp(\Delta F_0/RT)$

3.2.1 Thermal Conductivity Detectors

Thermal conductivity detectors (TCD) are a class of widely used detectors for gas chromatography. Their greatest assets are simplicity in operation and construction and universality of response. The two types of commercial TCDs are hot wire and thermistor detectors, and an additional type considered for this report is the polysilicon thermistor thermal conductivity detector.

All TCDs operate in substantially the same manner. A resistive element with a high coefficient of resistance change with temperature is physically placed in the output gas stream of the chromatograph and electrically connected in some form of bridge circuit. The bridge circuit is energized which causes the resistive elements to heat from dissipation of the applied power. This heating can be monitored by measuring the imbalance in bridge output voltage. Since the bridge imbalance is proportional to the temperature of the element which is in turn a function of the heat loss, any change in thermal conductivity of the carrier gas will produce a change in bridge imbalance. A more complete description of thermistor operation can be found in the book by Littlewood [5].

Helium is most often used as the carrier gas since it has a thermal conductivity of 2 to 8 times that of all encountered sample gases. There will then be a rise in temperature of the TCD during the passage of the peak through the detector regardless of the composition of the impurity. There is not the same vast range of sensitivities to different compounds which so drastically affects the operation of many ionization detectors.

The main difference between the two types of commercial TCDs mentioned above is in the form of the resistive element. The hot-wire TCD utilizes a filament, typically a tungsten alloy, which is often mounted coaxially in the output gas stream. The thermistor detectors typically utilize a commercially available bead thermistor of about 1-mm diameter hung by its lead wires in the center of the gas stream. The resistance and temperature coefficients of these two elements are quite different. The hot wire elements have resistances on the order of 100 Ω and temperature coefficients of about 0.4%/°C while the thermistors are more generally in the range of 10 kΩ with a change of 4%/°C. Thus for equal geometries the thermistor is more sensitive due to its higher temperature coefficient; however the bead geometry is not optimum for GC work as shown in Littlewood [6], so the response of the two elements is typically more equal.

The ultimate sensitivity of a TCD is usually limited by noise in the detector and by amplifier noise, since detection of one-ppm samples requires temperature measurement of microdegrees which corresponds to measurement of microvolt electrical signals. High quality integrated instrumentation amplifiers achieve this performance and will be discussed later. Using such amplifiers, performance at the 0.1-ppm level of butane in He is reported for a commercial hot-wire TCD.

The scaling problem associated with the TCD is probably the best understood of all the detectors since experimental information is available from the present miniaturized GC system operating with a 100-nl detector volume. This volume is larger than optimum due to the lack of availability of commercial thermistors with diameters less than 125 μm, and the problem in mounting such a small device in the output stream of the GC. Theoretically, the response of a miniaturized detector follows from the analysis given in Littlewood [7]. The geometrical factor, G, relates power dissipation, I^2R, to change in temperature of the detector, T, under changes in thermal conductivity, λ, as in

$$\frac{\partial T}{\partial \lambda} = - \frac{I^2 R}{JG\lambda^2}$$

where J is Joule's constant.

Since the thermal conductivity of the gas does not change with scaling and the heat loss I^2R is independently controllable assuming minimal changes in resistance with scaling, the geometrical factor controls the behavior of the detector with scaling. G is calculated through solution of Laplace's equation with boundary conditions appropriate for the geometry of the problem. In general, analytical solutions are only possible with simple geometrical shapes, and the two TCD geometries are simple enough to handle.

1) For a hot wire geometry with length l, wire radius r_2 and tube radius r_1:

$$G = \frac{2\pi l}{\ln(r_1/r_2)}$$

2) For the thermistor case with a spherical element of radius r_2 in a spherical cavity of radius r_1:

$$G = \frac{4\pi r_1 r_2}{r_1 - r_2}$$

It can be seen that G changes linearly with length changes of detector dimension. That is, if l, r_1, and r_2 all decrease by a factor of 10, G will also decrease by a factor of 10. Since $\partial T/\partial \lambda$ is proportional to G^{-1}, the sensitivity of the detector increases with decreases in size, but the maximum allowable power dissipation also decreases, so that increased sensitivity should not be immediately assumed. Since thermal conductivity detectors are true concentration sensing devices, they can be miniaturized without adversely affecting performance, which is an attractive property for a miniaturized system.

Integrated TC Detector--

In the majority of the column experiments to date, the thermistor configuration shown in Figure 9a has been used. The thermistor is sandwiched in a cavity between the glass and silicon wafers of the integrated capillary column with its leads emerging through holes etched through the

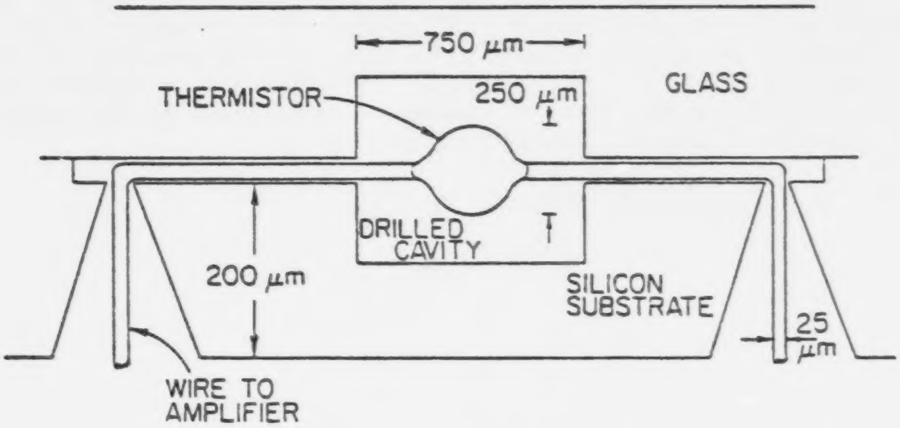
750 μm
THERMISTOR
250 μm
GLASS
DRILLED CAVITY
200 μm
SILICON SUBSTRATE
25 μm
WIRE TO AMPLIFIER

Figure 9a. PRESENT TCD CONFIGURATION.

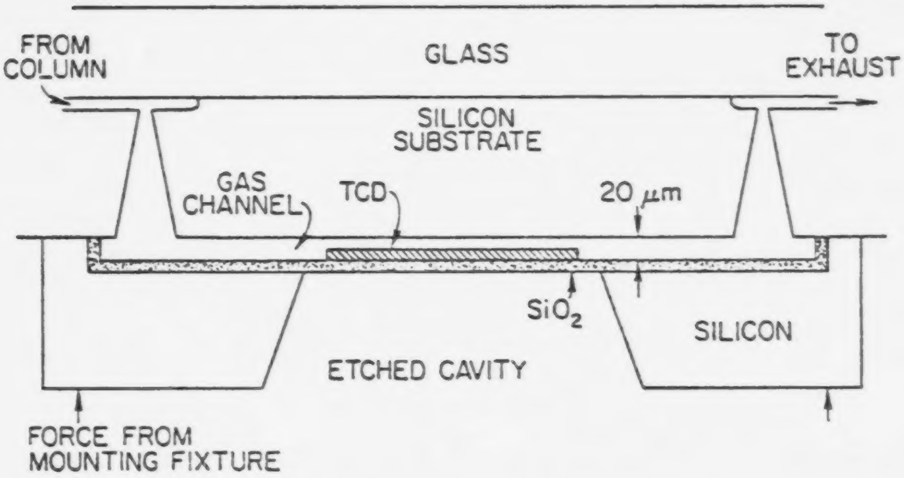
FROM COLUMN
GLASS
TO EXHAUST
SILICON SUBSTRATE
GAS CHANNEL
TCD
20 μm
SiO_2
SILICON
ETCHED CAVITY
FORCE FROM MOUNTING FIXTURE

Figure 9b. REPLACEABLE TCD CONFIGURATION.

silicon wafer. These holes are etched at the same time the gas orifice holes are etched, and the lead wire channels are etched during the column etch. The thermistor bead now most often in use is 250 μm in diameter with 25-μm diameter platinum-iridium lead wires. Since the column is only about 20 μm deep, a larger cavity must be provided for the bead. At present these cavities are made by ultrasonically drilling both the silicon and the glass. This process is not completely reproducible and does not have the accuracy of the other etch steps. While the configuration described above has proven useful for initial development, the volume of the drilled cavity is about two orders of magnitude larger than necessary, the lead wire arrangement is not optimum, and tedious manual alignment of the thermistor is required. These problems are expected to be remedied through the use of a precision replaceable detector.

Replaceable Detectors--
At present the thermistor is sealed in the detector cavity by the anodic bonding process. This sealing is nonreversible, and replacement of the detector implies replacement of the entire column. Thus for the next stage of development, replaceable detectors are a high priority item.

The general scheme for replaceable detectors is as follows. Since the silicon to glass sealing to form the column on the front side of the wafer is quite satisfactory, the replaceable detector should be located on the backside of the wafer, as are the valves. Feed-through holes will be etched from the back to front to allow the output gas stream to pass through the wafer; and the replaceable detector, on a silicon substrate, is attached to the back of the wafer as shown in Figure 9b. Such an arrangement is being used in the valve assemblies and represents currently available technology.

An advantage of the replaceable detectors is the possibility of batch fabricating the detectors. Since the detector assembly is only about 2 mm square, hundreds of detectors can be fabricated on a single 5-cm diameter silicon wafer using integrated circuit processing techniques. This should offer a very low cost detector if one of the integrated detector schemes described later in the report proves to be acceptable. Along with the batch fabrication possibilities, the detector will no longer be subjected to the rigors of the anodic bonding process, which involves 400°C temperatures, nor to the column lining process, which can involve concentrated acids. It will allow easier comparison between different detector designs under operation on the same column and the easy replacement of the detector if it ever fails during use. In addition, as was discussed in the column section, it was found that column lining material in the detector region adversely affected performance, and these replaceable detectors will not be installed on the column during column lining. Thus replaceable detectors are a high priority item for further development.

Detectivity of Present Thermistor Detectors--
The ultimate detectivity in any GC system is constrained by three main factors, amplifier noise, detector noise, and peak broadening. A sensitivity test was performed on the present column configuration to aid in the determination of the ultimate system detectivity using a thermistor detector. For this test the following set of parameters was used.

test gas: 4% isobutane in helium

carrier gas: helium

sample pressure: 1.76 kg/cm^2 (25 psi)

carrier gas pressure: 0.84 kg/cm^2 (12 psi)

injection time: 5 msec

In the present configuration 0.5 meter column, 250-μm diameter thermistor the output peak is 53 mV at the detector and is 200 msec wide (FWHM). This corresponds to 1.4 μV/ppm peak height.

Whether a 1 ppm sample can be detected is dependent upon whether or not the total system noise, referred to the detector, is substantially smaller than the signal. The thermistor noise is not easy to calculate theoretically, since it is always larger than Johnson noise for an equal valued resistor. Johnson noise for a 10 kΩ resistor at room temperature is 120 nV over a 100 Hz bandwidth. The thermistors seem to vary substantially in how close they come to this value, however units have been tested with peak to peak noise in the few microvolt range.

There are a number of low noise operational amplifiers on the market which would be useful in this application. A Fairchild unit, the μA725A, for example, has a maximum input noise voltage of about 150 nV and a maximum input noise current of 12 pA over a 10 Hz bandwidth. Since the source resistance of the thermistor circuit is about 2 kΩ, the input noise current is not significant.

In the present configuration, a sample of 10 ppm would be close to the lower limit of detectability due mainly to the uncertain thermistor performance. In the future, however, three improvements are possible. The first is a reduction in detector volume which would reduce the detector mixing time. Theoretically, 50-msec wide air peaks should be possible, which would increase the peak height in the isobutane example above by a factor of 4. The sensitivity would then be, for the same detector, 5.6 μV/ppm, and 1 ppm samples would be at the limit of detection. Second, advanced integrated detectors should match the geometries of the column more closely which should increase the sensitivity of the detector. Third, replaceable detectors would allow for better noise testing of either thermistor or hot wire detectors, along with the possibility of using detectors which are uncoated with column lining, which should improve noise performance.

These performance estimates are assuming that the flow noise of the carrier gas past the detector is minimal. The flow noise is dependent upon exact details of the geometry of the detectors and is quite difficult to calculate. Tests will have to be performed on the future replaceable detector configuration to assess the flow noise limitations.

Alternate TCD Configurations--

There are two types of TCD which are somewhat different from the commercially available devices and should be mentioned here. They are thermistors on silicon and polysilicon thermistors. These types of detectors rely on the capabilities developed at the Stanford University IC Lab for using selective etching of silicon to obtain thermally isolated structures.

Absolutely pure silicon, though classified as a semiconductor, at room temperature is, for all practical purposes, an insulator. Absolutely pure silicon, however, cannot now be made. There are always contaminants, in the parts per billion range and below, which tend to decrease the resistivity of the silicon. It is these impurities, in controlled amounts, which make large scale integrated circuits possible. It is these impurities which change the resistivity of the silicon substrate and allow resistors and transistors to be made. The resistors are the important devices for thermal conductivity detectors since they have non-zero temperature coefficients. The derivation of the temperature coefficient of resistivity for lightly doped semiconductors is beyond the scope of this paper (see for example, Grove [8] or Sze [9]), but for practical purposes, there is roughly an exponential dependence between the number of charge carriers available and temperature. Since the resistivity is roughly proportional to the number of available charge carriers, it is a strong function of temperature for lightly doped material.

The main problems in using such lightly doped material involve the small numbers of charge carriers involved. This small number (parts per billion) of impurities imply that resistors of approximately square geometry will have resistances on the order of megohms, and also that these devices will be susceptible to contamination during processing. The first problem can be easily handled simply by geometrical considerations while the latter depends heavily on the cleanliness of the available laboratory facilities.

The main thrust of these experimental TCDs is to place such a detector in the output gas stream utilizing the same technology as the remainder of the column and valve processing techniques. The present method of hand placing the commercial thermistor in a detector well is tedious, and non-optimum detector placement may easily result. The two new processing techniques make exact placement of the thermal element possible with no thermal penalty. The main problem in placing thermal detectors on a silicon substrate is in the extremely high thermal conductivity of the silicon compared to the carrier gas. Almost all of the heat is lost through the substrate and the detector becomes sensitive only to ambient temperature. This problem can be remedied by removing the silicon substrate around the detector by etching from the backside of the substrate. Such techniques, as diagrammed in Figure 10, have been developed during the past year.

The etched region can be filled with a material with low thermal conductivity, or it can be evacuated and sealed to produce a miniature vacuum chamber, which would have the lowest thermal conductivity. The supporting SiO_2 membrane is grown after the gas channel etch and is on the order of 1 μm thick. Membranes of linear dimensions 2000 μm x 100 μm have been made which reproducibly withstand conditions similar to those found at the output of a GC.

Initial efforts at the start of the contract period involved investigation of chemical vapor deposited silicon or polysilicon as the thermal element. Here the silicon was obtained from dissociation of SiH_4 at high temperatures with the subsequent growth of a multitude of single crystal silicon grains of about 1-μm size on a Si and SiO_2 substrate. The polysilicon was etched to form islands of 100 μm x 500 μm typical size which were insulated from the Si substrate by a 1-μm layer of SiO_2. A 5000 Å thick layer of SiO_2 was then thermally grown on the polysilicon. Figure 11a shows progress to this point.

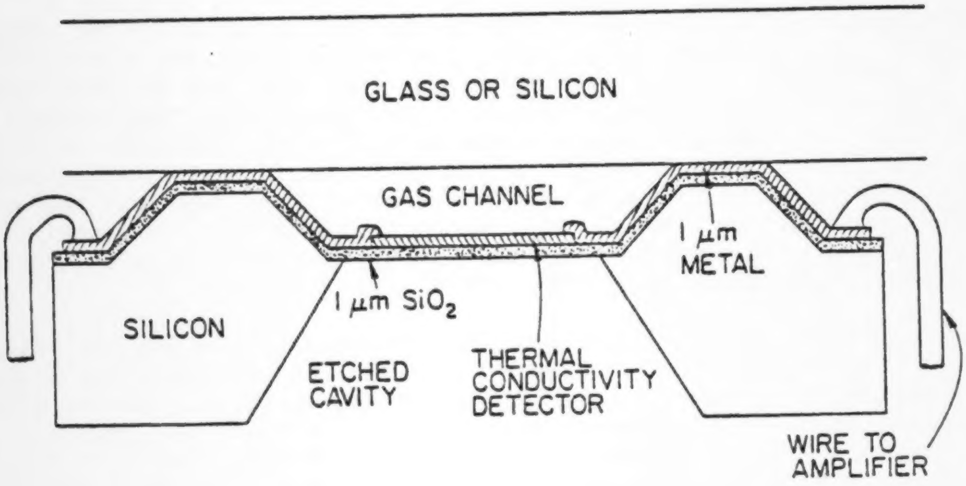
GLASS OR SILICON
GAS CHANNEL
1 μm METAL
1 μm SiO$_2$
SILICON
ETCHED CAVITY
THERMAL CONDUCTIVITY DETECTOR
WIRE TO AMPLIFIER

Figure 10. THERMALLY ISOLATED INTEGRATED DETECTOR.

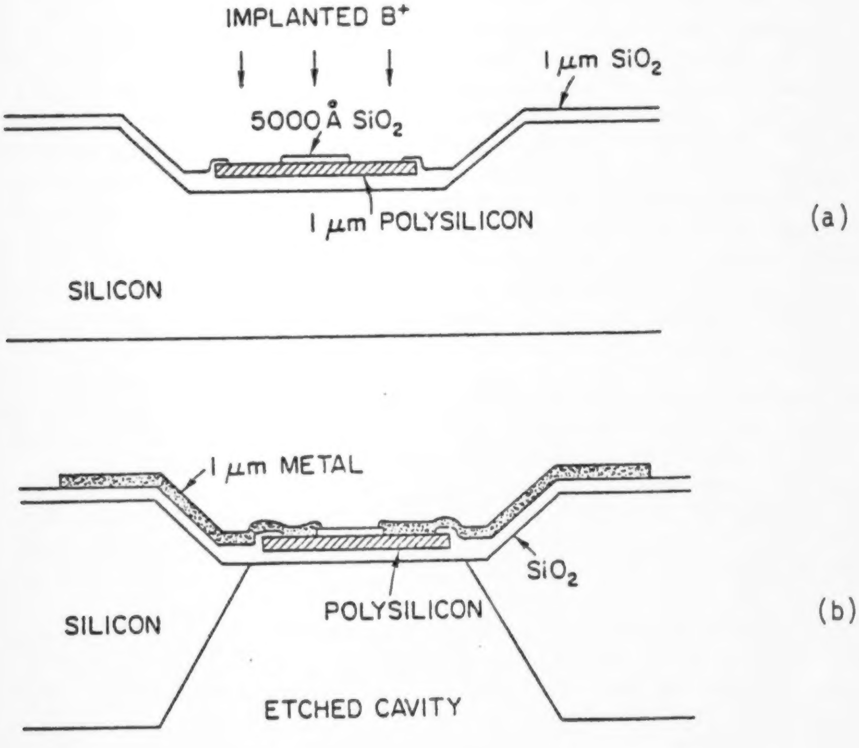
IMPLANTED B$^+$
1 μm SiO$_2$
5000 Å SiO$_2$
1 μm POLYSILICON
(a)
SILICON
1 μm METAL
SiO$_2$
SILICON
POLYSILICON
(b)
ETCHED CAVITY

Figure 11. CROSS SECTION OF POLYSILICON TCD
(a) At boron implantation stage
(b) Final device

Two parallel contact openings 10 μm apart were etched in the 5000 Å oxide along the length of the polysilicon island. The wafers were then ion implanted at varying energies such that the doping of impurities which penetrated through the oxide over the resistor region was about a factor of 10^3 less than the doping in the contact regions. Doping in polysilicon is not as predictable as in normal single crystal silicon since the polysilicon grain boundaries tend to both increase the effective diffusion constant of the impurities and also tend to trap impurities, so the number of electrically active impurities can easily be an order of magnitude less than the implanted dose. Thus such polysilicon doping is a mostly trial and error process. For these geometries, a dose of 10^{15} atoms per cm^2 at 100 keV was found to give the best results. During an anneal at 1200°C for 45 minutes, the doping in the contact areas diffuses toward the center of the resistor to further decrease the 10 μm resistor length. A standard aluminum metalization after silox protection completes the process. The completed structure is shown in cross section in Figure 11b. Polysilicon resistors of approximately 100 kΩ were made which had temperature coefficients of 2.5%/°C, much the same as thermistors. The noise performance was found to be in the millivolt range, however, which is unsatisfactory for TCDs. Such noise in polysilicon resistors is due to the large number of carrier traps associated with the polysilicon grain boundaries and seems unavoidable with this general processing scheme.

The next process to be investigated was the possibility of producing true thermistors on silicon substrates. Since the commercial thermistors perform adequately, thermistors produced in place offer the same advantages without the physical disadvantages associated with the commercial devices. Since an in-place thermistor is supported by the SiO_2 membrane, the need for relatively massive lead wires which decrease the performance of commercial devices is eliminated. The external support also makes possible substantially smaller volume thermistors, with the additional possibility of changing from an essentially spherical shape to one with a larger surface area to volume ratio.

Thermistors are made from a mixture of metallic oxides such as CuO, Mn_2O_3, NiO, FeO, CoO and others. These oxides are powdered and mixed to form a slurry. The slurry is applied to a support, two platinum-iridium wires in the commercial versions; and the assembly is fired at about 1000°C until the metallic oxides form a spinel type crystal configuration. This spinel acts like a semiconductor and produces resistors with high temperature coefficients. A more complete description can be found in a book by Sachse [10]. The thermistor fabrication is even more of an art than silicon processing, and useful processing data is lacking in the literature. The additional complications involve a reduction in volume of about 10^2 over the smallest commercially available thermistor along with construction on a metallized substrate. After substantial trials, a method of platinum metallization was developed which involves sputtering through an etched silicon mask. This produces high quality platinum metallization on the silicon substrate with dimensional tolerances commensurate with the other fabrication dimensions. The thermistor slurry is then placed over this metallization. The density of the slurry is chosen such that there is about a 10 to 1 reduction in volume of the slurry during drying, which minimizes the problem of localizing such a small 100-picoliter volume of thermistor material.

After firing, the thermistors have temperature coefficients of about 3%/°C and noise performance equivalent to commercial thermistors. Resistances have to this point been rather high, about 1 MΩ. This is due primarily to the wide metallization spacing used to this point. Now that the metallization scheme has been more fully developed, resistances in the 10 kΩ to 100 kΩ region should be readily attainable, which would make this technique useful.

Conclusion--
It thus appears feasible to use a modified thermal conductivity detector in a replaceable holder in the final system configuration. The ultimate detectivity of the system will be limited by the detector to the few part per million range which should be adequate for the purposes of the unit. The necessary modifications are extensions of presently available technologies and are more development than research efforts.

3.2.2 Alternate Detector Technologies

Early gas chromatographs used thermal conductivity detectors for essentially the same reasons that they were used in the development of the miniaturized system. Eventually, however, alternate detector types were found to offer increased performance at the expense of more complicated construction and operation. The most widely used of these alternate technologies utilize ionization properties of the sample gases to realize an electrical signal which is related to the passage of sample gas molecules. A number of the more promising detector types are discussed below, including how they are thought to operate if miniaturized to the same scale as the rest of the system. There are a vast number of other detector schemes such as pyroelectric, capacitive, ion selective FET, and sonic detectors which were investigated and found to be unacceptable for use in the miniaturized system due to power, size, and sensitivity problems and will not be discussed in this report.

Flame Ionization Detector--
The flame ionization detector has become the most common detector in gas chromatography for the detection of organic species. It operates by mixing the column effluent with H_2 gas and air and igniting the mixture to produce a flame. The flame jet is typically grounded, the impurities in the GC output stream are ionized by the flame, and the resultant ions are collected as a current [11]. The collection efficiency is close to 100% and the current is roughly proportional to the number of carbon atoms in the sample [12]. Typical performance figures are linear dynamic range of 10^6 and 10^7 and detectivities of at best 10^{-12} to 10^{-11} g, which corresponds to about 10^{10} molecules of propane.

The response to a wide variety of organic impurities makes the flame ionization detector useful in a similarly wide variety of applications. For the miniaturized system, however, the difficulties in shrinking the size of the detector are immense. Present FIDs occupy the same volume as the entire miniaturized system, even if the additional gas supplies are neglected. The detector is usually run between 100 and 400°C which would be difficult to achieve in a battery powered device. The burner is a precision machined assembly with intricate gas paths and insulated collectors.

Present FIDs have H_2 gas flows of about 30 ml/min which would have to be scaled down to match the 60 μl/min flow rate typical of the miniaturized system.

Another problem involves the scaling of sensitivity of a FID. The present systems have, as mentioned above, detectivities of about 10^{10} molecules of sample. The miniaturized system is constrained to have sample sizes on the order of 1 nl which corresponds to about 5.6×10^{13} molecules/injection. Thus present detectors of macroscopic size would be limited to detecting only 10^{-3} concentrations at best, and the FID does not seem to be a realistically achievable detector for a miniaturized GC system.

Electron Capture Detector--
The electron capture detector, ECD, has gained wide acceptance in the field of gas chromatography due to its extraordinary sensitivity to certain classes of halogenated hydrocarbons. A comprehensive review of ECD theory can be found in an article by E.D. Pellizzar [13]. As is the case with all detectors, the important points relate to how the behavior of a type of detector will scale with decreases in volume of about three orders of magnitude.

A typical commercial ECD uses an intense radioactive source to produce a multitude of low energy electrons in the GC output stream. The presence of an electron capturing species in the carrier will tend to decrease the concentration of electrons in the ECD. The periodic application of an electric field collects the more mobile electrons without collecting the less mobile, negatively charged ions. The positively charged carrier gas molecules and negatively charged sample molecule recombination rate is about 10^6 higher than the electron-positive ion recombination rate [14], so the low energy electrons tend to remain free until collected by the pulsed field.

A typical commercial ECD is reported to have a 1 Curie tritiated scandium source in a cell volume of 180 μl [15]. The size constraints on the miniaturized GC restrict a detector cavity to about 10 nl -- more than 4 orders of magnitude smaller. The design criteria for commercial detectors are therefore not directly applicable. For example, the use of tritium or Ni^{63}, two of the most common β^- sources, is not possible in the miniaturized system, since β^- particles produce only 10^2 to 10^3 ion pairs per centimeter of travel in the air [16], and in the 50 μm maximum column depth there would be only about one ion pair produced per β^- decay. This is certainly very inefficient. A miniaturized system would thus be forced to use an α particle source such as Th^{228}, Ra^{226}, or Am^{241}. These sources are more attractive in the miniaturized system since α particles have typical energies on the order of 5 MeV compared to the tens of keV for β^- particles, and thus produce about 10^5 ion pairs per centimeter of travel, or about 500 ion pairs in the 50-μm detector distance.

The large number of ion pairs produced per α decay leads to possible noise problems. The output signal of an ECD is, in effect, a decrease in current. Random decreases in current caused by noise will be interpreted as signal, and since the output of decay particles from a radioactive source is a stochastic process, the noise behavior from such a source is predictable.

Exactly how this decay noise will effect the operation of a miniature detector is not as clear. An indication is given by a simple noise analysis, paralleling that of Pellizzari. If we assume that the maximum size radioactive source which can be used is 200 μm x 200 μm x 5 μm, which would just fit in an acceptable detector volume, and the use of pure Th^{228} which is one of the most intense α sources available, then the maximum total amount of material is 2×10^{-7} cm^3. Since Th^{228} has a half life of about two years, and there are four other α particles released over a four-day period from the decay products of Th^{228}, then there are about 6×10^8 α decays per second from the source. This corresponds to a 8-mCi source.

Now the noise current i is given by the Shot equation

$$i = [2e(a + 1)\ I_0 B_\omega]^{1/2}$$

where

e = charge of an electron, $1.6 \times 10^{-19}C$

I_0 = number of α particles emitted per unit time

a = pairs per decay event

B_ω = amplifier bandwidth

Substituting, assuming an amplifier bandwidth of 100 Hz which is necessary to observe 100 msec type peaks, the noise current is approximately $i = 1.2 \times 10^{-12}A$. If the minimum detectable signal is twice the noise, then the detectable electron depletion is

$$\frac{de^-}{dt} = 1.8 \times 10^7\ \frac{e^-}{sec}$$

If the electron capture efficiency is 100%, which is thought to be achievable with molecules with extremely high electron attachment coefficients such as SF_6, then the minimum detectable flow of solute molecules is

$$\frac{dN}{dt} = 1.8 \times 10^7 \text{ molecules per second.}$$

Now under a peak with full width at half maximum (FWHM) T and peak concentration n_p, the total number of molecules

$$N_t = 1.064\ n_p T.$$

Assuming 200-msec peaks with $n_p = 1.8 \times 10^7$

$$N_t = 3.6 \times 10^6 \text{ molecules.}$$

Now with one-nl sample injections at the one-ppm level at two atmospheres, there are 5.6×10^7 solute molecules per injection, just slightly more than the 3.6×10^6 minimum detectable sample. Thus under most optimum conditions, one ppm input concentration of samples such as SF_6 or CCl_4 would be detectable, but gases with lower electron capture coefficients would not be observable at the 1 ppm level.

In addition to the α particles, the 8-mCi source emits a variety of radiation. The most damaging is the 2.6 MeV γ-ray from the thallium-208 to lead-208 transition. This corresponds to about a 100 mrem/hr radiation exposure if the device is worn next to the body. Such exposure is excessive by anyone's standards, and effectively eliminates this type of ionization detector from consideration.

Argon Detector--
The argon detector was introduced by Lovelock in the late 1950's as a possible alternative to the FID or TC detector. A more complete analysis of the operation of the argon detector was subsequently made by Knapp and Meyer [17]. Essentially the detector operates by utilizing a radioactive source particle such as from H^3 or Ni^{63} to excite Ar carrier gas atoms. The argon atoms have a number of excited states in the 10 to 15 eV range including an ionization potential of 15.76 eV and two metastable levels at 11.72 eV and 11.54 eV. These metastable levels have appreciable lifetimes and, at least under conditions of low solute concentrations, are the predominant mechanism for solute ionization. That is, the argon metastables ionize molecules with ionization potentials under 11.5 eV through collision processes known as Penning ionization.

There are two important considerations as to the utility of such detectors for miniaturized operation. The first is ultimate detectivity and the second is dynamic range. The ultimate detectivity is set by the maximum ionization efficiency and the detector noise, while the dynamic range is constrained in this type of detector by the maximum number of argon metastables which are available, which limits the maximum number of solute molecules which can be ionized. There are various ways in which argon detectors can be operated which depend on how close to breakdown voltage the device is run. These considerations are not particularly important for this analysis, since the range of currents encountered for a constant solute concentration rarely change by more than an order of magnitude over regions of practical interest.

The reported range of ionization efficiencies is from 1×10^{-6} to 3×10^{-5} [18-20]. These efficiencies were observed under a wide range of detector size and electrode configurations. Unfortunately, for the miniaturized detector there are only 5.6×10^7 solute molecules available in a 1-nl injection of a 1-ppm sample. There would then be only 1700 electrons available assuming the maximum conceivable efficiency. This represents only 2.8×10^{-16} coulombs of charge, or a 280-μV signal on a 1 pF integrating capacitor. While such performance might be possible using extraordinarily sophisticated electronics, it is hard to image how such performance could be attainable in a hand-held package. Such currents would also have to be visible through detector noise. As in the ECD, the argon metastables would have to be produced through the use of an α source such as Th^{228}. Since there are about 10^8 α decays during a 100-msec peak, the stochastic emission process implies that there would be variations of that

α emission on the order of 10^4 decays per peak. The α particles are charged, and if that charge were collected, it would swamp the 1700 electrons obtained from the solute molecules. Even if the α particles were shielded from the detector electrodes through geometrical considerations, the argon ion to argon metastable ratio is not low enough to completely neglect the Ar^+ background current. Thus it appears highly unlikely that operation near the 1 ppm level is feasible for a miniaturized detector.

The Th^{228} source mentioned above produces some 5×10^{10} excited Ar atoms during a 100-msec peak. The maximum possible signal, assuming operation outside of the multiplication region, would be obtained if every excited Ar atom ionized a sample molecule. Since there are about 5.6×10^{13} molecules per injection, a 0.1% sample would overwhelm the detector. If a more reasonable but very optimistic ionization efficiency figure of 1×10^{-3} is assumed, then the detector would saturate at 1 ppm, a figure which is already in the noise. Thus the prospects of using such a detector are slim at best.

Breakdown Voltage Detector--
As may readily be imagined from the previous discussions, the introduction of a small amount of a gas with lower ionization potential into an inert carrier gas with a relatively high ionization potential will drastically alter the electrical properties of the carrier gas. The one electrical parameter which can easily be measured without worrying about the particular ionizing reactions taking place in the mixture is the breakdown voltage.

There has not been extensive research into breakdown voltage detectors in the past for two main reasons. The first is the highly nonlinear response in breakdown voltage with impurity gas concentration. This makes simple integration of peak areas very difficult without computational facilities. Second, reproducibility of breakdown voltage is somewhat suspect, although little practical information applicable to 50-μm electrode spacings is available in the literature. Most of the research has been with inert gas mixtures such as argon in neon. Here neon is the gas with the high ionization potential with a metastable state at approximately the ionization potential of the argon. Thus this mixture is similar to something like propane in argon. Typical sets of breakdown voltages with impurity concentration are graphed in a book by Weston [21]. These graphs show that there is variation in breakdown voltage from 1500 to 400 V in the range from 1 ppm to 1000 ppm of argon in neon. The data shown is for a pressure-electrode spacing product of 450 cm-torr, which is substantially higher than the 5 cm-torr typical of a miniaturized detector. At 5 cm-torr the total change in breakdown voltage is only from 175 V to 110 V, and the maximum change takes place at the 10^{-4} range [22]. While the magnitude of the voltage is more in the measurable range, the compression of the effect makes it less desirable than at larger electrode spacings. Also, small changes in electrode properties over time are more likely to be a problem with small area electrodes.

It is likely that similar operation with hydrocarbons in an argon carrier would be possible, especially considering the information such as in the article by Knapp and Meyer on the operation of argon detectors at near breakdown levels. For mixtures of propane in argon from 0.3×10^{-5} to 148×10^{-5} parts per volume, the breakdown voltage of their detector changed from 1300 to 500 V [23]. The electrode spacing was on the order of 5 mm, which is equivalent to the argon in neon conditions in the Weston book.

The electronic and data handling requirements are more severe with a breakdown voltage detector. A high voltage ramp would be necessary with circuits to detect the onset of breakdown. This breakdown voltage would have to be converted to concentration by the microprocessor. The conversion would likely be difficult for each impurity, which increases the amount of calibration data required by the microprocessor. The main advantage of such a detector is the ease in construction of a prototype unit, for such a prototype would be necessary to obtain information on the stability of the effect with time, temperature, and cleanliness of the detector electrodes.

Photo-Ionization Detector--
The photo-ionization detector (PID), through technological advances, has recently become competitive with the FID and ECD in the detection of picogram quantities of sample with laboratory instruments. A PID utilizes photons from an ultraviolet light source to either directly ionize solute molecules or to create carrier gas metastables which then ionize the sample molecules through collision processes. The chief advantages of a PID involve the use of the light source instead of the hydrogen-oxygen flame in the FID, or the radioactive sources in ECD or argon detectors. Essentially, light offers a cleaner ionization source which minimizes background current. From the standpoint of the miniaturized system, however, the light source draws considerable power, on the order of a watt in conventional systems, and for stability purposes probably has to be run continuously. A radioactive source does not have this same power consideration.

The two principal UV sources which have been investigated utilize glow discharge lamps operating with either H_2 or Ar gas. The UV photons result from electronic transitions between atomic energy levels, and thus the spectrum of light output consists of light energy only at fairly specific energies. The principal resonance emission lines of interest are the H_2 Lyman-α line at 10.20 eV and a pair of Ar lines at 11.38 eV and 11.62 eV. A more complete table can be found in Wentworth, et al [24]. The simplest way to produce such a lamp is by a high voltage discharge through the gas at a pressure of about 200 μm of Hg. There is a problem, however, in directing the UV photons to the region of interest. Most materials absorb strongly in that region and do not make good windows. Lithium floride is transparent to about 11.9 eV light, and thus is the most commonly used window material. Of the two lamps, the H_2 source is generally recognized to be the simplest to construct and operate.

A H_2 lamp suffers from a potential problem. The 10.2 eV photons are not capable of directly ionizing sample molecules with ionization potentials greater than 10.2 eV. Species with higher ionization potentials include substances such as methanol, methylene chloride, aliphatic hydrocarbons below C_6, and 1,2-dichloroethane. This potential problem may not be important if the class of compounds of interest does not include any of the high ionization potential molecules. If an Ar lamp is used, the list of molecules with higher ionization potentials is sharply reduced, with methane being the sole undetectable hydrocarbon. It is also possible to include a TC detector in series with a more exotic detector such as a PID to partially compensate for the latter's specificity.

The scaling for a PID is easily calculated if certain assumptions are made. Essentially the only assumption is that the flux density of UV photons is comparable to that in a large lamp. For a commercial detector (HNU Systems, Inc., Model PI 51-01) with detector volume 0.25 cm^3 and flow rate of 30 cm^3/minute, the sample transit time is 8 msec, while for the miniature detector with 5-nl detector volume and flow rate of 1 μl/second, the transit time is 5 msec. Since the time spent in the detector is comparable and since the assumed flux density is constant, then the ionization efficiencies of the two detectors can be expected to be the same. The published efficiency of the commercial detector is 8×10^{-4} [25]. With a 1-nl injection of a 1-ppm sample there are 5.6×10^7 solute molecules injected. With an efficiency of 8×10^{-4} there would be 4.4×10^4 electrons available for detection. With a peak width of 0.2 seconds, this corresponds to a current of 3.2×10^{-14}A or a voltage of 6 mV on a 1 pF capacitance. Both of these numbers are small, but are probably attainable with sophisticated electronics. The noise current of the commercial detector is listed as 4×10^{-14}A. It is not obvious how this number would scale with decreasing volume, but since high quality insulation materials are available utilizing integrated circuit techniques, it is likely that comparable noise performance can be obtained.

There has not, to our knowledge, been any work on extremely small UV light sources. Since the detector volume of the miniaturized system is 50,000 times smaller than the commercial detector, it is certainly conceivable that the 1 watt lamp power input can be substantially reduced. Assuming a 4 watt-hour battery supply and approximately 5% of the battery power is available to operate the detector, then about 0.025 watts would be available to operate the UV light source. The feasibility of producing such a lamp has yet to be determined although details of producing miniaturized, quartz-coated gas cavities with integral electrodes has already been developed at the Stanford University IC lab. Whether such cavities can be utilized as UV light sources remains an area of further study, and it seems to be the determining factor for producing a useful miniaturized PID. It appears that the PID is the most promising ionization detector for use in the miniature system.

Ionization Detector Conclusion--
Most ionization detectors are limited by the extremely small number of sample gas molecules in an output peak. Combined with the low ionization efficiency of most of the detectors, the resulting output signal will be too small to measure in the miniature system for most of the schemes. The photo-ionization detector is the only type which is reasonably general in its response and has low enough noise to make the small signals easier to detect. A photo-ionization detector would probably be used in series with a thermal conductivity detector so that the best features of both detectors

could be used. A considerable effort would be necessary to miniaturize the ultraviolet light source used in the photo ionization detector.

3.3 SAMPLE COLLECTION AND INJECTION SYSTEM

The function of the sample injection system is to collect atmospheric gas samples and inject precisely controlled amounts of the sample as short pulses into the carrier gas stream at the inlet of the column. The extremely small volume of liquid stationary phase in the miniature capillary column, the small volume of the column itself, the low carrier gas flow rate, and the limited amount of carrier gas available in a pocket-sized device impose the following requirements on the sample injection system.

1) The volume of injected pulses must be on the order of one nanoliter.

2) The duration of the sample pulse as it enters the column must be a few milliseconds.

3) The sample injection system itself must not use more than a few microliters per minute of carrier gas.

4) The size of the valves must be acceptable for use in a pocket-sized device.

Since there are no commercially available sample injection systems, or even miniature valves, which are small enough in size, have small enough dead volumes, and can inject small enough samples to meet the above requirements, we have focused our attention on miniature valves and injection systems integrated on the silicon wafer along with the capillary column. These integrated structures certainly offer the compact size and the nanoliter volumes required of the injection system.

The sample collection system need not be of such small volume as the injection system since it can deliver substantial amounts of gas to the injector compared to the final injected nanoliter pulses. The main requirements for the collection system are that it deliver fresh atmospheric samples to the injection valves and that it be small enough to fit in the pocket-sized package.

The following subsections detail the design considerations for the integrated valves, an evaluation of those valves, a brief description of several alternate valve actuation methods, and an evaluation of two feasible schemes for realizing a miniature sample collection and injection system for the pocket-sized gas analyzer.

3.3.1 Miniature Integrated Valves

The miniature valves which have been fabricated at Stanford University as part of this investigation have clearly demonstrated the feasibility of integrated silicon valves for the miniature gas analyzer. The valves can either be fabricated separately or integrated on the same silicon wafer as the capillary column. They are currently designed to have less than

10-nl dead volume, and with cycle actuation times of less than 500 μsec, the valves are capable of injecting the desired nanoliter samples into the GC column. The valves appear to be leak-free when monitored with the TC detector at the output of the column. Several valves have been put through 100,000 operations in air with no change in performance.

The miniature valves are simple, solenoid-actuated diaphragm valves. As shown in cross section in Figure 12, the valve consists of: 1) an etched

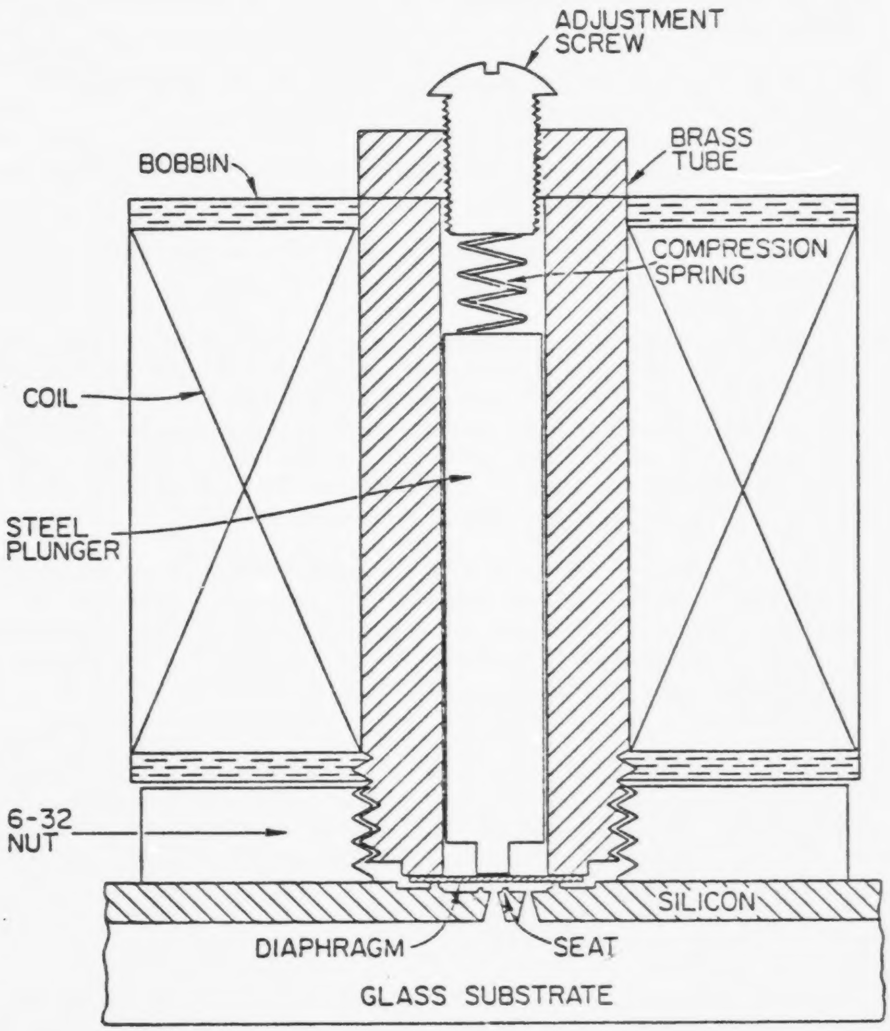
ADJUSTMENT SCREW
BOBBIN
BRASS TUBE
COMPRESSION SPRING
COIL
STEEL PLUNGER
6-32 NUT
SILICON
DIAPHRAGM
SEAT
GLASS SUBSTRATE

Figure 12. CROSS SECTION OF SOLENOID ACTUATED INTEGRATED SILICON VALVE.

silicon seat and orifice, 2) a Parylene* coated nickel diaphragm, and 3) a solenoid actuator and plunger assembly. Botn the solenoid assembly and the diaphragm are removable, to facilitate cleaning of the internal valve areas.

The valve shown in Figure 12 is a normally closed ON/OFF valve. The force exerted by the plunger on the diaphragm is sufficient to deflect the diaphragm tightly against the valve seat, thus preventing any gas from flowing through the orifice. This static force of approximately 10 grams-force (gf) is adjustable by means of the finely threaded adjustment screw and the compression spring. When the solenoid is energized, the plunger is pulled into the coil, allowing the diaphragm to relax and gas to flow over the valve seat. The diaphragm is continually pressed against the outer "sealing" ring by the brass solenoid tube to seal off the gases in the interior of the valve and prevent them from escaping outside of the valve.

Valve Fabrication--
The body of the miniature valve is fabricated from silicon in a series of photolithography and silicon etching steps. It consists of the valve well, sealing ring, seating ring, and orifice as shown in Figure 13. The 3-mm diameter of the valve well and 2-mm diaphragm diameter were chosen to be compatible with the standard 6-32 machine screw threads on the end of the solenoid tube.

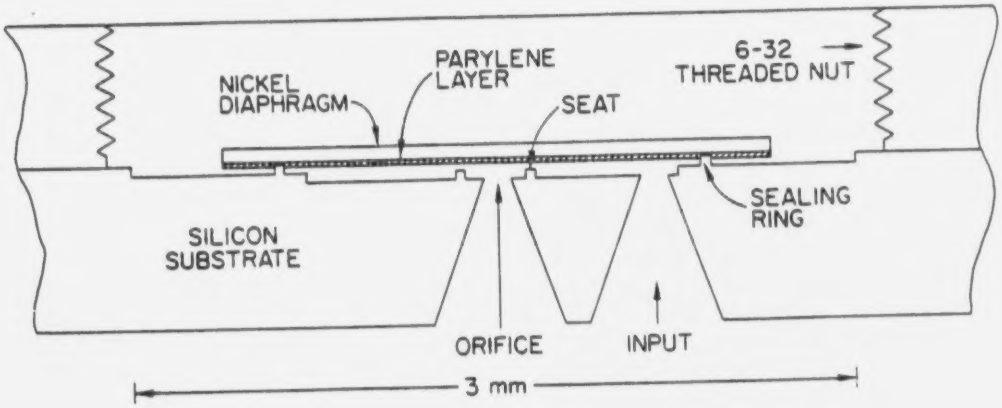

Figure 13. CROSS SECTION OF INTEGRATED SILICON VALVE.

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*Parylene is the trade name for a vapor deposited para-xylylene polymer developed by Union Carbide Corp.

The circular valve well is first etched 10 μm down into the silicon leaving only the 1.8-mm diameter sealing ring remaining at the surface level of the silicon wafer. Next, the floor of the well is etched another 5 μm deeper, leaving the 300-μm diameter seating ring raised 5 μm above the silicon floor. Both the seating and sealing rings are 30 μm wide and serve as knife-edge seals when pressed into the pliable Parylene surface of the diaphragm. The 10-μm depth of the seating ring was chosen to allow only 5 μm of clearance and deflection of the diaphragm. The 5-μm height of the valve seat is sufficient to allow good penetration of the seat into the Parylene diaphragm, while minimizing the dead volume of the valve orifice.

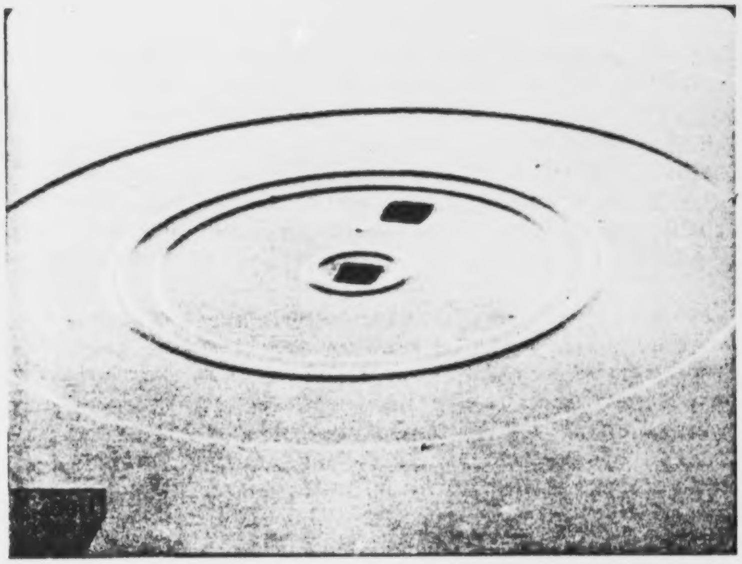
The final step in the fabrication of the silicon body of the valve is the etching of the orifice and input gas holes through the silicon wafer from the back side. An anisotropic silicon etch is used in this step to yield small-volume holes. The effective dead volume of the output side of the valve is essentially the volume of the orifice, approximately 6 nl. The input dead volume consists of the input hole and the space between the sealing ring and seating ring, a total of 10 nl. Figure 14 shows SEM photographs of a completed silicon valve well.

The thin silicon diaphragms used in the original valve design [1] have been replaced by Parylene-coated nickel diaphragms. These diaphragms consist of 2-mm diameter, 12-μm thick electroformed nickel disks formed with one extremely smooth side. A 5-μm thick Parylene layer is vapor deposited on the smooth surface of each diaphragm. The diaphragm is placed in the valve well (Parylene side down) and is clamped in place by the threaded brass solenoid tube. If the diaphragm ever becomes grossly deformed, punctured, or dirty, it can easily be removed and replaced.

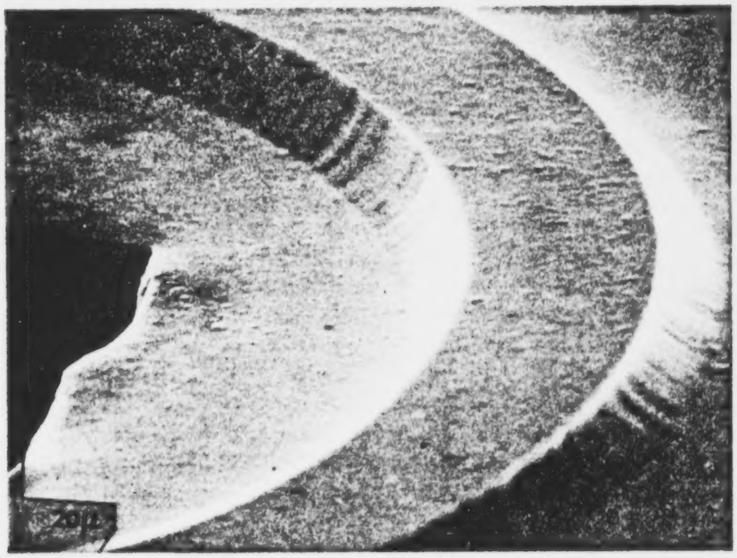
The nickel-Parylene diaphragm was chosen to fulfill two structure requirements. First, the diaphragm must be sufficiently springy for it to pull away from the valve seat when the pressure from the solenoid plunger is released. Nickel is an ideal metal for this application since it has a relatively high elasticity (Young's modulus $2 \times 10^{+10}$ dynes/cm^2) and it can easily be electroformed into the diaphragm shape. Secondly, the diaphragm must be capable of forming a gas-tight seal with the valve seat and sealing ring. These etched silicon structures have sub-micron size imperfections (peaks and pits) on their sealing surfaces which prevent the unyielding silicon and nickel surfaces from mating perfectly. The additional 5-μm thick Parylene layer used on the valve diaphragms serves as a slightly deformable gasket which accommodates the irregular surfaces and results in a gas-tight seal and a leak-free valve. The fact that the silicon seats are knife-edge structures also aids in the formation of gas-tight seals. The seating force between the diaphragm and seat is concentrated on the knife-edge area and reaches as much as 7.8 kg/cm^2 (110 psi). This force is sufficient to push the silicon seat well into the Parylene layer.

Valve Actuation--

There are a wide variety of actuation schemes for the miniature valves: pneumatic, solenoid, electrostatic, magnetic, piezoelectric, thermo-expansive, and fluidic, to name just a few. Most of these schemes, however,



Valve well -- approximately 40X magnification.



Detail of valve seat -- approximately 800X magnification.

Figure 14. SEM PHOTOGRAPHS OF ETCHED SILICON VALVE WELL.

are not practical for the miniature system due to size and power restrictions.

The valve actuator which has proven most feasible is the miniature solenoid shown in Figure 12. The 7-mm diameter, 10-mm high solenoid coil is wound on a nonmagnetic brass tube which has been machined with 6-32 NC threads on the outside of one end and 0-80 threads through the end cap on the opposite end. The open end of the brass tube is ground flat to provide an even force on the diaphragm and sealing ring when it is screwed down against the silicon wafer. A standard 6-32 nut aligned over the valve well and epoxied in place serves at present as the mounting fixture for the solenoid.

The plunger consists of a 1.5-mm diameter steel rod machined on one end to a 0.375-mm diameter. The plunger is held against the valve diaphragm by a tungsten compression spring with a force of approximately 10 gf. An 0-80 machine screw threaded through the brass end cap is used to set the position and compression of the spring to achieve the desired 10 gf.

The solenoid actuators described above were fabricated and tested on miniature silicon valves. When energized, the solenoids overcame the 10 gram force of the compression spring and pulled the plungers sufficiently far from the diaphragms (greater than 5 μm) to allow the valves to open. The minimum open-close cycle time of the valves was approximately 200 microseconds. These solenoid valves were operated up to 120,000 times without the need for readjusting the force-setting screw.

The 120 watts of power required to operate the present solenoid valve is, however, way above acceptable limits. The 0.12 joules of energy expended, mostly as heat, during a 1-msec long valve actuation is sufficient to slightly heat the silicon wafer and thus show up as a spurious detector response. Though this problem is severe, we are confident that it can be overcome. The efficiency of the solenoid can be greatly increased with the addition of high-permeability magnetic return paths illustrated in Figure 15. Such a design would keep the magnetic field dispersion in air to a minimum and thus result in much more efficient use of the generated magnetic flux. As an example, IMC Magnetic Corp. makes a miniature solenoid (4SD819-3) which is only 9.5 mm in diameter and 23 mm long. Their unit produces a plunger force and stroke comparable to our solenoid, yet requires only 180 milliwatts of power. Modification and use of the IMC solenoid or realization of the solenoid design of Figure 15 should yield a miniature valve actuator of acceptable size and efficiency for use in the pocket size GC system.

Alternate Actuation Methods--

Pneumatic actuation--Several of the other more plausible valve actuation schemes are shown in Figure 16. Of all of these, only the pneumatic actuation method has been tried and proven feasible though not satisfactory. In this case, the diaphragm is deflected against the seat by gas pressure applied to the back side of the diaphragm. This control pressure is either vented or applied to the diaphragm by an "external" two-way solenoid valve. The ON/OFF cycle time of this valve is limited by the speed

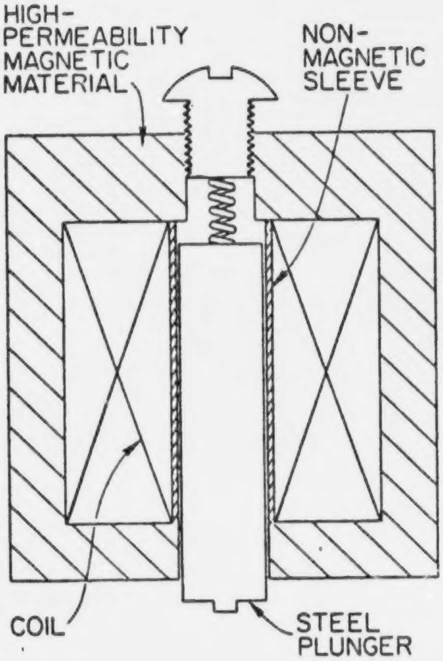
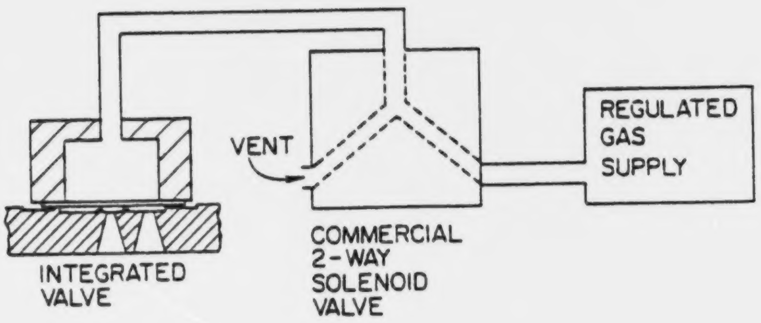


Figure 15. CROSS SECTION OF SOLENOID WITH MAGNETIC RETURN PATHS.

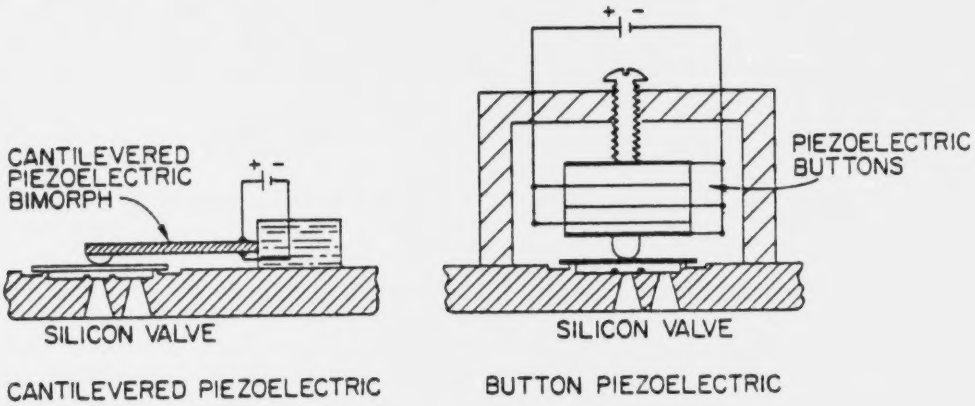
of the external solenoid valve and the delay caused by filling and venting the length of tubing between the miniature valve and the external valve. Using a subminiature commercial solenoid valve (Skinner valve #BIDA9200), the observed minimum cycle time was 20 milliseconds, two orders of magnitude longer than with direct solenoid actuation. The pneumatic system also has the disadvantages of requiring the large external valve (2.5-cm diameter x 5-cm length for the Skinner valve) and requiring a high pressure [typically 2.81 kg/cm^2 (40 psi)] gas supply and regulator to provide the control pressure. The addition of these two components in the already crowded package of the pocket-sized device is not at all desirable.

Piezoelectric actuation--The piezoelectric actuator shown in Figure 16b is based upon the electromechanical properties of a long cantilever-mounted piezoelectric beam or bimorph. When a voltage on the order of 100 volts is applied between the two sides of the bimorph, it bends downward, pressing against the diaphragm and closing the valve. In practice, this scheme is severely limited by the amount of force which the bimorph can generate against the diaphragm. Typical bimorphs 3.5 cm in length are only capable of exerting less than one gram force; far less than the 10 gram force necessary to operate the diaphragm valve.

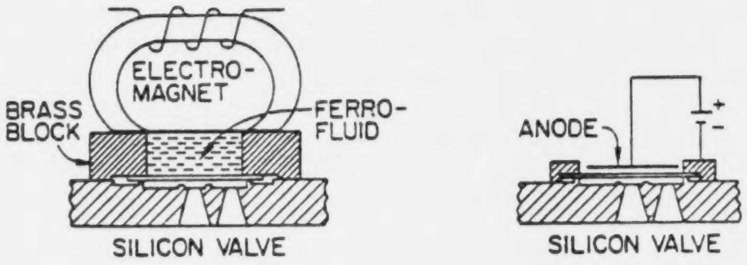
As an alternative to the cantilevered beam, a stack of piezoelectric buttons could be mounted directly above the diaphragm. When energized, the stack would expand, forcing the diaphragm downward against the valve seat. The major drawback in this scheme is that the vertical expansion of the


VENT
REGULATED GAS SUPPLY
INTEGRATED VALVE
COMMERCIAL 2-WAY SOLENOID VALVE

(a) Pneumatic actuation.


CANTILEVERED PIEZOELECTRIC BIMORPH
+ -
SILICON VALVE
CANTILEVERED PIEZOELECTRIC
+ -
PIEZOELECTRIC BUTTONS
SILICON VALVE
BUTTON PIEZOELECTRIC

(b) Piezoelectric actuation.


ELECTRO-MAGNET
BRASS BLOCK
FERRO-FLUID
SILICON VALVE
ANODE
+
-
SILICON VALVE

(c) Magnetic actuation. (d) Electrostatic actuation.

Figure 16. ALTERNATE ACTUATION SCHEMES FOR INTEGRATED VALVES.

stack is only a few micrometers, thus requiring extreme precision in the positioning of the stack and the diaphragm. This critical positioning aspect of the design makes the piezoelectric scheme far more difficult to realize than the miniature solenoid actuator.

Magnetic actuation--The magnetic valve actuation method shown in Figure 16c utilizes a magnetic ferrofluid and a strong magnetic field to exert pressure on the valve diaphragm. The ferrofluid is essentially a colloidal suspension of 20-200 Å diameter single domain magnetic particles in a liquid carrier. The internal pressure of the liquid can be increased by a divergent magnetic field as:

$$\Delta P = 1/4\pi \int_0^H MdH$$

where H is the applied magnetic field and M is the magnetization of the fluid [26,27]. This increased internal pressure at the liquid-diaphragm interface appears as a pressure differential across the diaphragm and can be used to deflect the diaphragm against the seat. As in the case of pneumatic actuation, a pressure differential of roughly 2.81 kg/cm^2 (40 psi) is required for reliable valve closure. Utilizing a ferrofluid with a magnetic saturation of 350 gauss, a magnetic field of 60 kilogauss would be required to produce the desired pressure on the diaphragm. An electromagnet capable of producing such an intense magnetic field with the geometrical constraints imposed by the flat silicon and glass wafers could not be fabricated small enough to be compatible with the size of the miniature valve. In addition, to realize a normally closed valve, a continuous current flow through the electromagnet would be required. The static power consumption and the size of the electromagnet thus eliminate the magnetic system as a feasible actuator for the miniature valves.

Electrostatic actuation--The simple electrostatic attraction scheme sketched in Figure 16d has also been suggested as a means of valve actuation. In this case, however, an electrostatic force sufficent to move the diaphragm could not be generated with the configuration of the miniature diaphragm valve. As an example, if we assume a circular diaphragm and anode plate 2 mm in diameter and spaced 6 μm apart (allowing for 5 μm diaphragm movement), the initial pressure of 2.81 kg/cm^2 required to move the diaphragm would require an applied potential of 1,500 volts. This is derived from the equation for the attractive force between two plane parallel capacitor plates:

$$f/A = \frac{V^2 \varepsilon_0}{2d^2} \quad \text{(force/unit area)}$$

where

ε_0 = permittivity of free space

d = spacing of the plates

V = applied voltage

This 1.5 kilovolt potential could not be maintained since the breakdown potential of the air in the 6 μm gap is on the order of 100 volts. Breakdown of the air would result in a continuous arc and loss of any attractive force between the plates.

Fluid Logic Gas Sampling Valve--

A system of fluidic logic elements (NOR gates and check valves) has also been proposed as a miniature gas sampling system for the integrated gas chromatograph. Fluidic logic is accomplished by steering gas streams in small channels by means of a series of gas jets and vent holes. A sample injection system for a gas chromatograph has been proposed by Wade and Cram [28] and is sketched in Figure 17. This large scale system consisting of four discrete fluidic logic elements was shown to be capable of injecting 3.6-μl samples into a GC column. However, miniaturization and integration of this system for use with our small GC system is not viewed as promising for several reasons.

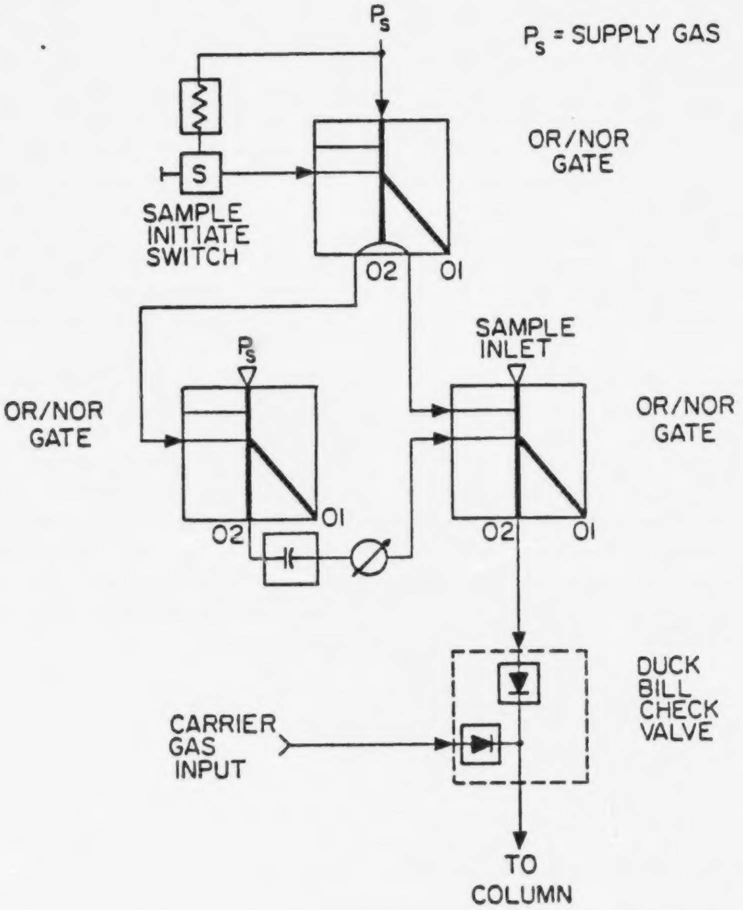

P_s
P_s = SUPPLY GAS
OR/NOR GATE
S
SAMPLE INITIATE SWITCH
O2
O1
P_s
SAMPLE INLET
OR/NOR GATE
OR/NOR GATE
O2
O1
O2
O1
DUCK BILL CHECK VALVE
CARRIER GAS INPUT
TO COLUMN

Figure 17. THREE OR/NOR FLUIDIC SAMPLE INJECTION SYSTEM.

1) The discrete fluidic logic elements which are currently available are based upon specific geometries such as jets with perfectly square orifices, right angle channel intersections with vertical walls, and circular holes. Fabrication of the devices on the silicon wafer with the capillary column using our silicon etching technology would preclude the use of those well defined geometries.

2) Further miniaturization of the fluidic devices from their current dimensions makes some of the design assumptions invalid, thus necessitating further research into the basic fluid dynamics of these 1 to 10 μm sized devices.

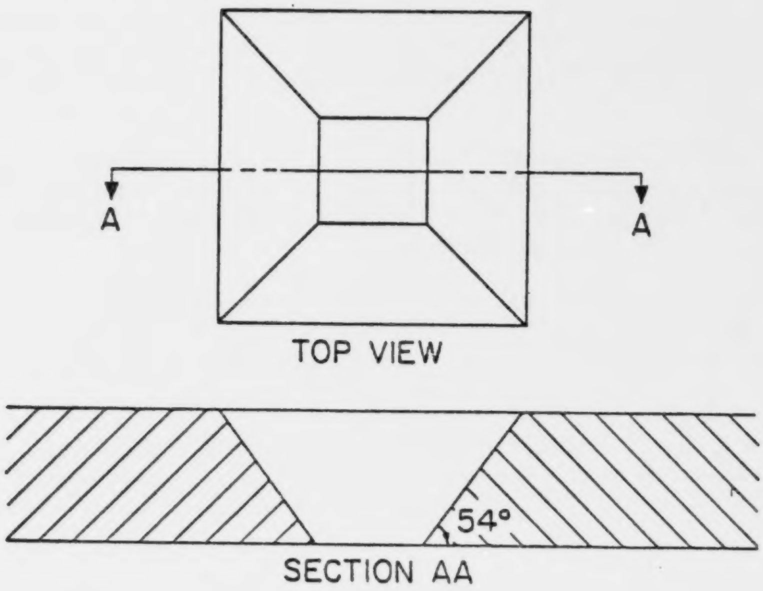
3) Substantial amounts of gas are used to drive steering jets in the fluidic logic elements. This gas is lost to the system and may represent too large a gas consumption for the pocket-sized device.

4) As in the case of pneumatic valve actuation, a separate gas supply would be required, and an external solenoid valve would also be necessary to initiate the sampling sequence of the fluidic system.

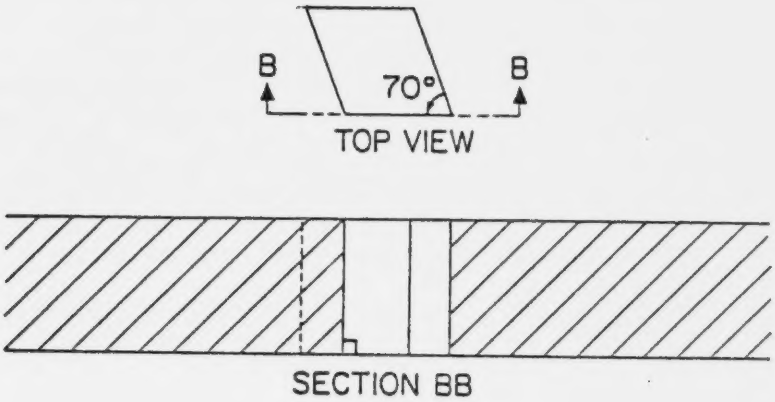
Design and Fabrication Improvements in Miniature Solenoid Valves--
Our experimental work with the miniature valves has lead to the conclusion that several improvements in both design and fabrication procedures are necessary to produce high-yield, reliable, and efficient solenoid-actuated miniature valves.

1) In an attempt to reduce the dead volume of the valves, the orifice and input gas holes through the silicon wafer which contribute to most of the dead volume should be reduced in volume. By simply reducing the orifice dimensions to 50-μm square, our current design of feedthrough holes (shown in Figure 18a) can be reduced to 4.6-nl volume. If the feedthrough hole is formed using an anisotropic silicon etchant and a (110)-oriented wafer, the anisotropically etched hole will have the geometry shown in Figure 18b, and will have a volume of only 0.4 nl. Thus by using (110)-silicon wafers and by changing the shape of the holes, the volumes of the feedthrough holes associated with the valves can be reduced by an order of magnitude.

2) For the miniature valve to be used as a high-pressure valve in the pressure regulator system, the overall diaphragm area will have to be reduced. With the current dimensions of the valve, the force exerted on the solenoid plunger by the high gas pressure (force = pressure x diaphragm area within the sealing ring) would be 25 grams-force for a 35 kg/cm^2 (500 psi) carrier pressure. Such a plunger force is too high for the miniature solenoid. By reducing the valve dimensions by a factor of two, a more reasonable plunger force of 6 gf would be sufficient to maintain valve closure.


A
A
TOP VIEW
54°
SECTION AA

(a) (100) surface orientation.


B
B
70°
TOP VIEW
SECTION BB

(b) (110) surface orientation.

Figure 18. ANISOTROPICALLY ETCHED HOLES IN SILICON.

3) As in the case of the removable detector, it would be desirable to be able to fabricate the valves completely separate from the columns. This process would allow many valve seats to be fabricated at once on a silicon substrate and later cut apart, thus reducing the number of processing steps involved in production of the capillary column wafer and improving the yield of working valves. One possible scheme for producing these valves is shown in Figure 19. Utilizing the small-volume feedthrough holes, the dead volume of this valve would only be increased by 1 nl over that of a completely integrated valve. The most difficult aspect of this design, and the process which has not yet been perfected, is the anodic bonding of the valve chip to the substrate wafer via an intermediate 20-μm thick glass layer. A similar bonding procedure has been demonstrated [29], so this valve design is deemed to be feasible.

4) As discussed in the valve actuation section, the efficiency of the solenoid actuators has to be increased by the addition of magnetic return paths.

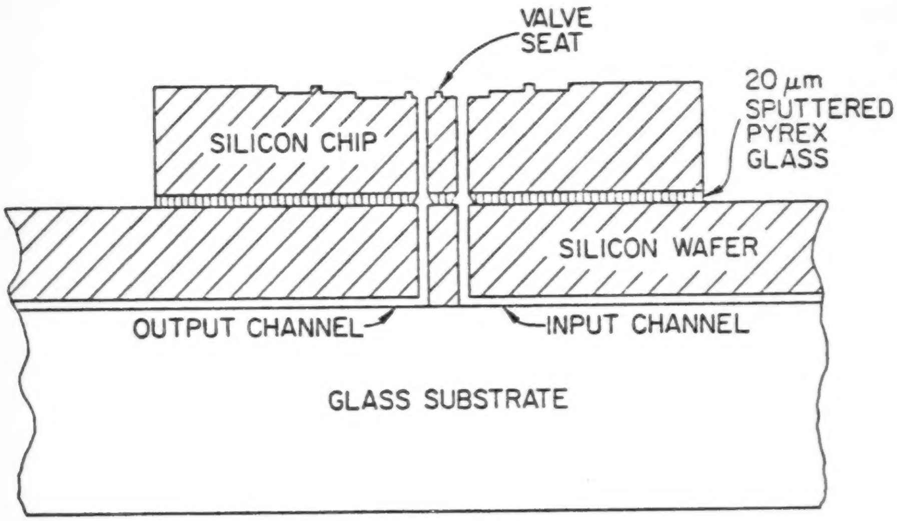


Figure 19. CROSS SECTION OF SEPARATELY-FABRICATED SILICON VALVE SEAT ATTACHED TO SILICON/GLASS SUBSTRATE.

3.3.2 Sample Injection Systems

Using the miniature silicon valves as basic building blocks, a sample injection system can be designed and integrated on the silicon wafer along with the capillary column. The feasibility of two such systems, along with appropriate means of sample collection, has been investigated. The simplest injection system consists of a single miniature valve and a servo-driven pump for sample collection. An alternate injector uses five miniature valves and an aspirator pump to draw sample into the valving network. Both of these injection schemes will be detailed in the following sections.

One-Valve Injection System--
The one-valve injection system is the simplest injection scheme that we have devised for the miniature GC system. It has been utilized in all of our experimental work to date. A schematic diagram of the system is presented in Figure 20. It consists of a single normally-closed ON/OFF valve integrated with the capillary column and a piston pump to draw in and pressurize the atmospheric sample. The carrier gas normally flows through a high resistance gas path, past the output of the ON/OFF valve, and into the capillary column. With the valve closed, fresh sample gas is circulated through the input side of the valve. When a sample is to be injected, the pressure of the sample gas on the input side of the valve is raised above that of the carrier gas, and the valve is opened briefly. A plug of sample thus flows through the valve and forces its way into the carrier gas capillary. The high resistance gas path upstream of the valve prevents the sample from traveling too far upstream and out of the integrated gas channel. When the valve closes, carrier gas flow returns, sweeping the sample pulse into the capillary column. The amount of sample gas injected is a function of the sample and carrier gas pressures, and the length of time that the valve is held open.

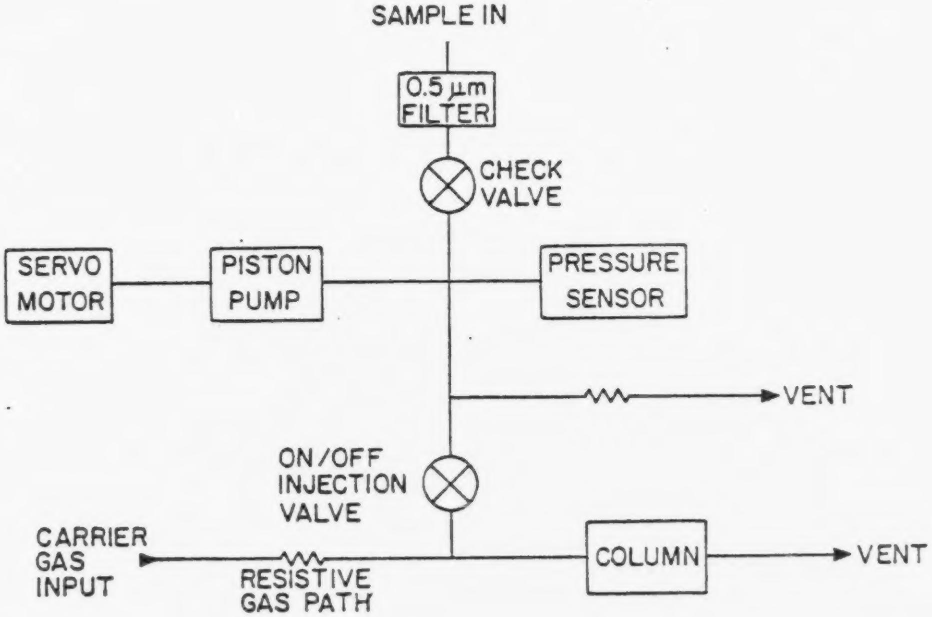


Figure 20. ONE-VALVE INJECTION SYSTEM.

The integrated portion of the injection system is shown in cross section in Figure 21. The miniature valve is fabricated on the opposite side of

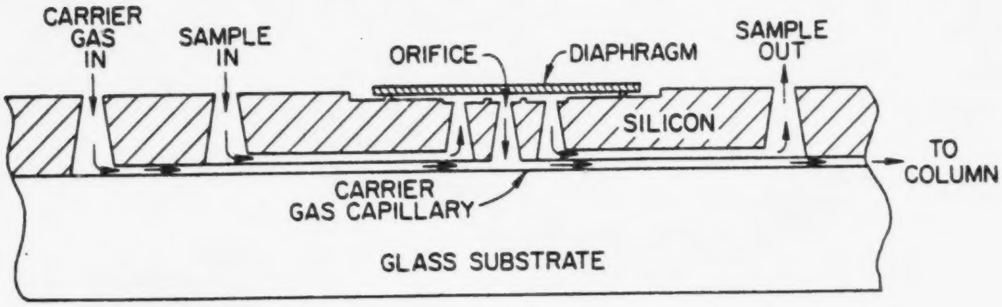


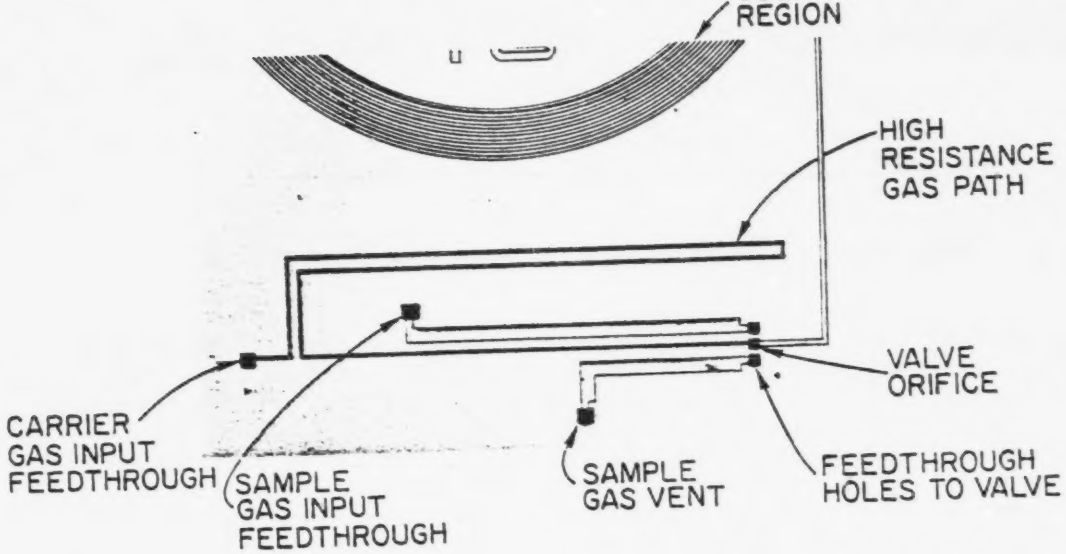
Figure 21. CROSS SECTION OF INTEGRATED ONE-VALVE INJECTION SYSTEM.

the silicon wafer from the capillary column so that the dead volume between the valve and the carrier gas capillary is minimized. In this case, that dead volume is simply the 6-nl volume of the valve orifice. The resistance path upstream of the valve is realized by a long section of narrow capillary channel. Figures 22a and 22b are labeled photographs of the injection system portion of a miniature chromatograph. The injection configuration shown was utilized in most of our column evaluation experiments. The injector proved to be capable of injecting reproducible sample pulses as small as 1 nl in volume. Figure 23 is an oscilloscope photograph showing a family of air peaks as they evolved from a 0.5-m capillary column. The fact that the peak widths are relatively constant as the amount of injected sample is increased indicates that the injected pulses are sufficiently narrow as to have little effect on the column efficiency and width of the output peaks.

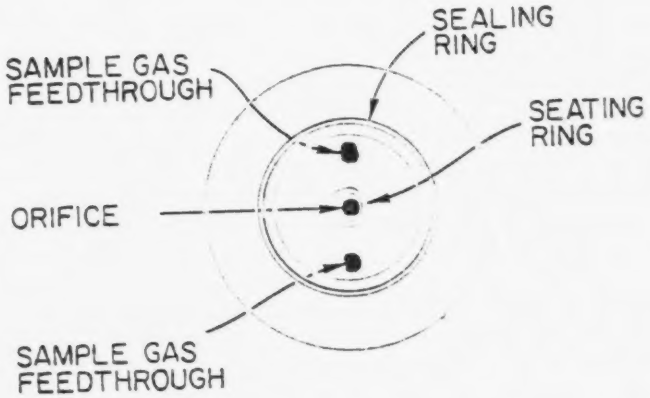
The price paid for simplicity of the integrated part of the injection system is increased complexity of the sample collection unit. The collection system must perform two operations: 1) draw fresh atmospheric samples into the instrument, and 2) pressurize the sample gas to a specified pressure, possibly up to 2.8 kg/cm^2 (40 psi), at the input of the ON/OFF valve. One possible realization of the system (shown in Figure 20) consists of a piston pump, check valve and pressure sensor. These devices do not have to be as miniaturized as the integrated valving system; however, they do have to be small enough to fit in the pocket-sized instrument.

Figure 24 is a full-scale drawing of a proposed pump system utilizing a 0.25-cm^3 syringe, a miniature servo, a flapper-type check valve, and an integrated pressure sensor. The total space occupied by this system is only 4 x 6 x 1.5 cm, and the estimated current consumption at 4.5 volts is 75 mA-seconds per injection, or 10 mA-hr per eight-hour work day. With reference to Figure 20, operation of the system can be described as follows.

The piston is normally fully in the pump until a sample is to be drawn. As the servo withdraws the piston, 0.2 cm^3 of air is sucked from the outside of the instrument through the filter and check valve. The filter will most likely be a 0.5-μm Millipore unit which will serve to keep


COLUMN REGION
HIGH RESISTANCE GAS PATH
VALVE ORIFICE
CARRIER GAS INPUT FEEDTHROUGH
SAMPLE GAS INPUT FEEDTHROUGH
SAMPLE GAS VENT
FEEDTHROUGH HOLES TO VALVE

(a) Front side, approximately 5X.


SEALING RING
SAMPLE GAS FEEDTHROUGH
SEATING RING
ORIFICE
SAMPLE GAS FEEDTHROUGH

(b) Back side, approximately 25X.

Figure 22. PHOTOGRAPHS OF A MINIATURE GC SYSTEM WITH COMPONENTS OF THE SAMPLE INJECTION SYSTEM LABELED.

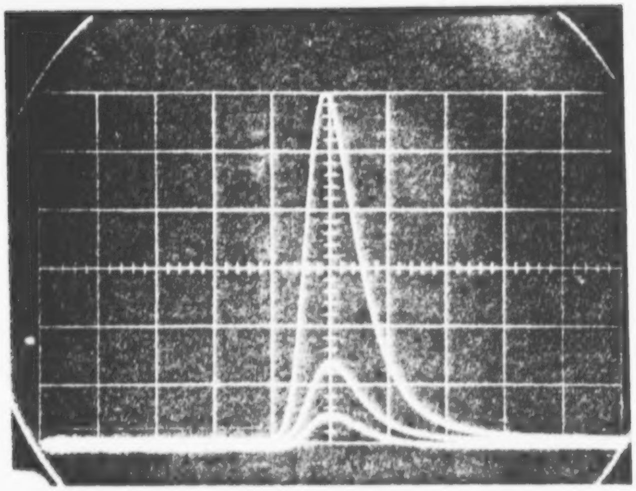
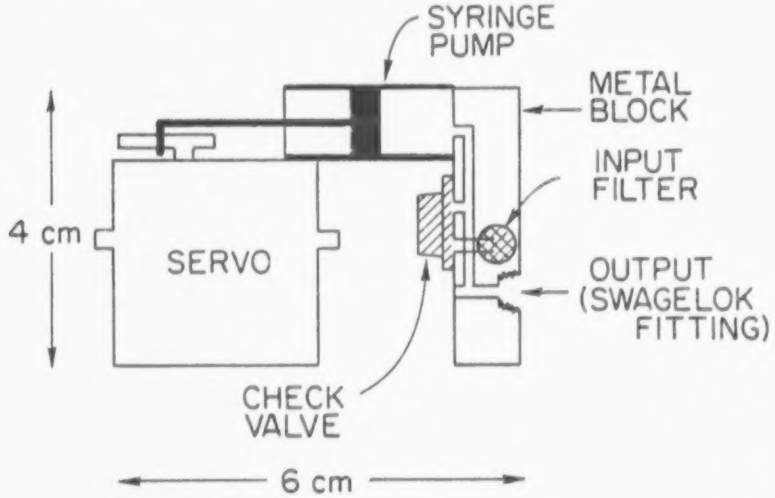


Figure 23. FAMILY OF AIR INJECTED PEAKS MONITORED AT THE OUTPUT OF A 0.5-m COLUMN. 600 μsec, 1.5 msec, 6 msec injection times.



SYRINGE PUMP
METAL BLOCK
INPUT FILTER
4 cm
SERVO
OUTPUT (SWAGELOK FITTING)
CHECK VALVE
6 cm

Figure 24. FULL SCALE DRAWING OF SAMPLE PUMP SYSTEM.

particulate matter out of the GC system. When the piston reaches its maximum stroke, the servo reverses. With reverse gas flow, the flapper check valve closes, forcing pressure and gas in the syringe pump to bleed out through the high resistance path of the integrated valve. When the pressure reaches a predetermined value (as monitored by the pressure sensor), the ON/OFF valve is actuated, injecting the sample into the column. The servo continues pushing the piston into the pump, and during the minute or so time between samples, all of the sample gas pressure is bled off through the valve resistance.

Though the miniature pump system has not yet been assembled and evaluated with the miniature GC, all of the component parts are available and appear to be adequate for the unit. A Cannon Micro-Mini servo is capable of exerting 2 kgf force on the piston while drawing only 75-mA current. Both glass and plastic syringes are available which can easily generate 2.8 kg/cm^2 (40 psi) pressures with a 1-cm stroke. The integrated pressure sensor developed at Stanford University is only 1 mm x 1 mm x 0.2 mm in size and is capable of measuring 2.8 kg/cm^2 pressures with a resolution of 1.4 x 10^{-3} kg/cm^2 (0.02 psi). It also appears feasible to produce a tiny flapper-type check valve using a metal plate and a flexible Parylene flap as shown in Figure 25. The check valve and pressure sensor could be mounted together in a structure on the end of the syringe pump.

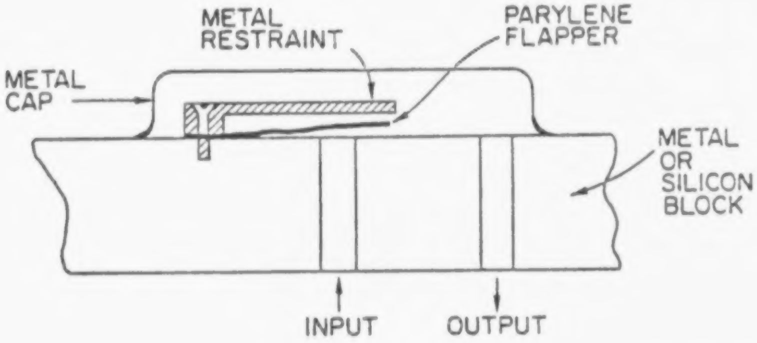


Figure 25. CROSS SECTION OF A PROPOSED FLAPPER CHECK VALVE.

5-Valve Sample Injection System--

The 5-valve injection system is essentially a sample collection system and injecting system all integrated together on the silicon wafer with the miniature capillary column. The only component which is external to the wafer is the Millipore filter at the inlet port of the instrument. This arrangement greatly simplifies the external connections of the system at the cost of having to realize five perfectly working valves on the same wafer.

The five ON/OFF valve system has been proven to be realible and of adequate performance, since NASA utilized this system in the two chromatographs which they landed on Mars. A schematic diagram of the miniature integrated system which we would propose for our GC is shown in Figure 26. It consists of three normally open and two normally closed ON/OFF valves and an integrated jet pump on the output of the column. During normal operation the carrier gas is directed into the capillary column while sample gas is pumped from the atmosphere, through the sample collection chamber, and out through the pump and column output. When a sample is to be injected, all valves change state simultaneously, thus isolating the sample chamber from the outside world and sweeping its contents into the column with carrier gas. The amount of sample injected into the column is equal to the volume of the sample collection chamber.

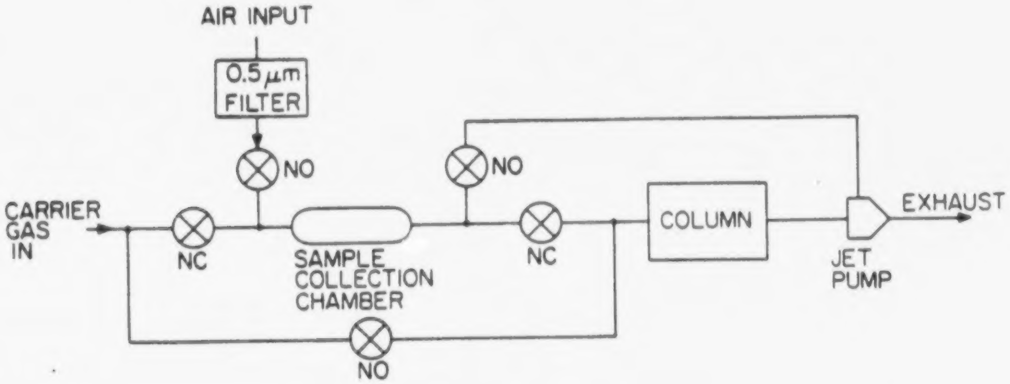


Figure 26. SCHEMATIC OF 5-VALVE INJECTION SYSTEM. NO -- normally open solenoid valve; NC -- normally closed solenoid valve.

Realization of the integrated 5-valve system requires the development of two components which have not yet been built: the normally open ON/OFF valve, and the integrated jet pump. The normally open valve simply requires reconfiguration of the solenoid actuator such as shown in Figure 27. In this valve, the plunger is normally held away from the diaphragm by a tension spring and adjustment screw. When the solenoid is energized, it overcomes the spring tension (approximately 10 gf) and pulls the plunger farther downward into the coil and against the diaphragm. Though the principles involves are the same, this valve actuator will be much more difficult to realize in practice than the normally closed valve due to the critical dimensions of the plunger and the attachment of the tension spring.

The integrated jet pump sketched in Figure 28 is based upon the fluid interactions which occur as a high velocity fluid jet enters a large area of low velocity fluid. The high velocity fluid in the jet mixes with that of low velocity surrounding it and the velocity of the jet is gradually lowered as the distance from the nozzle is increased. Because the velocity reduces as the distance increases, the width of the jet must increase in order to maintain the initial value of momentum. The result is that mass flow increases and fluid is drawn into the jet by this "entrainment" process [30]. This extra flow is provided by the gas surrounding the jet, thus creating pockets of low pressure which serve as a pump when vented to the outside world.

Large jet pumps or aspirators such as described above are in common use and can pump liters per minute of fluid. To function satisfactorily as

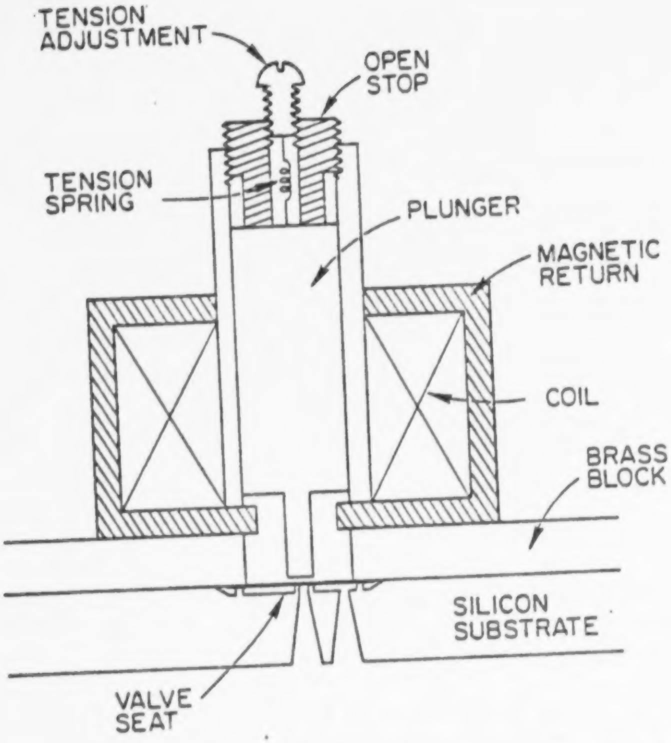

TENSION ADJUSTMENT
OPEN STOP
TENSION SPRING
PLUNGER
MAGNETIC RETURN
COIL
BRASS BLOCK
SILICON SUBSTRATE
VALVE SEAT

Figure 27. CROSS SECTION OF NORMALLY OPEN VALVE.

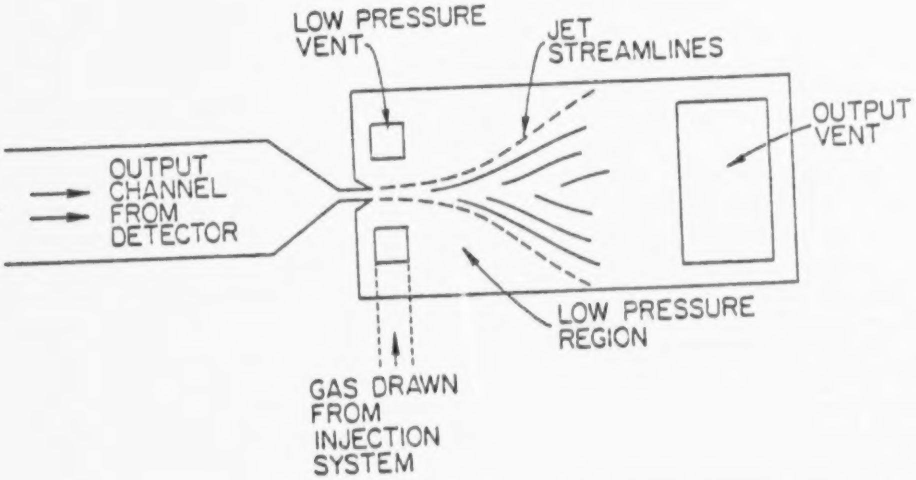

LOW PRESSURE VENT
JET STREAMLINES
OUTPUT VENT
OUTPUT CHANNEL FROM DETECTOR
LOW PRESSURE REGION
GAS DRAWN FROM INJECTION SYSTEM

Figure 28. INTEGRATED JET PUMP ETCHED IN A SILICON WAFER (top view).

a pump for the integrated injection system sampling once per minute, the pump need only draw about 10 μl/min pumping action with a carrier gas jet typically flowing at 60 μl/min.

3.4 ELECTRONICS

The electronics portion of the miniature system handles the control, data collection, and numerical analysis functions of the miniature gas chromatograph. The design is complicated by the size and power constraints of a hand-held, battery operated system. While the circuits have not been designed in detail, the devices to be used appear to have the required performance, and the entire detailed design should be a difficult but straightforward project. The following discussion covers the amplifier, analog to digital conversion, microcomputer, control, and display systems which are envisioned to be used in the miniaturized system.

3.4.1 Detector Amplifier

The amplifier portion of the miniature system is the most capable of utilizing commercially available components and standard circuit configurations. The amplifier must boost the output signal of the detector and, in conjunction with the microprocessor, deal with drift problems. For the purposes of this discussion it is assumed that thermistor detectors will be used; hot wire detectors would require essentially similar electronics, but an ionization detector would use a substantially different front end.

There are three main ways to provide the power necessary to self-heat a thermistor detector. They are referred to as constant voltage, constant current, and constant temperature. The constant voltage scheme uses a standard Wheatstone bridge with from one to four thermistors in the arms of the bridge. The configurations with multiple detectors minimize drift and have twice the sensitivity, but the one thermistor detector arrangement is used at present in the miniature GC for simplicity. The availability of the computer makes the drift problem less important, and when replaceable detectors with negligible dead volume are developed, a two-thermistor detector can easily be used.

A simplified form of a constant voltage detector is shown in Figure 29. Current flow through the thermistor arm of the bridge heats the thermistor. Any change in the thermal conductivity of the thermistor environment will cause a change in temperature of the thermistor which is detected and amplified. A problem with this configuration is related to the passage of the air peak in the column. The air peak has lower thermal conductivity than the He carrier and the temperature of the thermistor rises dramatically during its passage. If the thermistor does not recover quickly, then subsequent peaks may be hard to detect. In the constant voltage configuration the resistor in the lower arm of the bridge acts as a current limiting element.

A constant current detector is shown in Figure 30. Here, of course, the current limiting is absolute, and thermal excursions are minimized, since

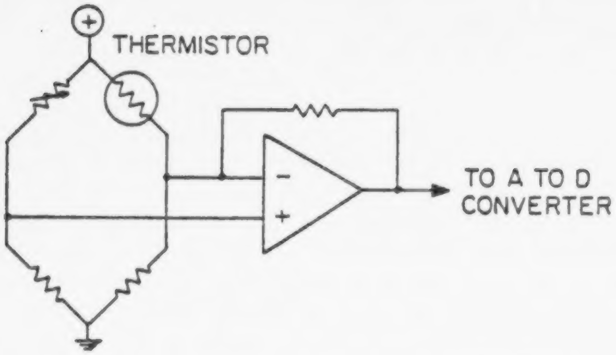

THERMISTOR
−
+
TO A TO D
CONVERTER

Figure 29. CONSTANT VOLTAGE DETECTOR.

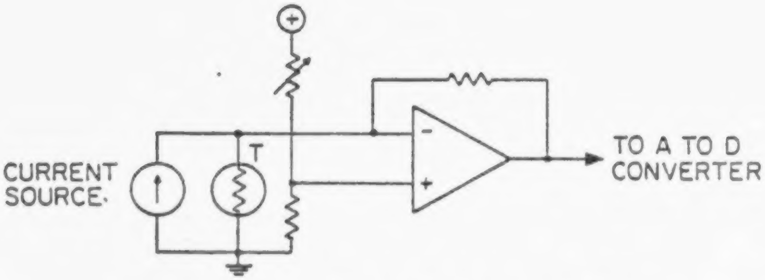

CURRENT
SOURCE
T
−
+
TO A TO D
CONVERTER

Figure 30. CONSTANT CURRENT DETECTOR.

the power dissipation of the thermistor is $I^2R(T)$. The resistance of the thermistor decreases with increases in temperature, thus power dissipated also decreases with temperature increases which limits the maximum temperature. In this circuit, however, noise at the output of the current source is directly amplified, so current noise must be kept to under 1 μA, which is difficult to routinely achieve in a pocket-sized instrument.

The constant temperature configuration is shown in Figure 31. This circuit adjusts the voltage across the thermistor until the thermistor

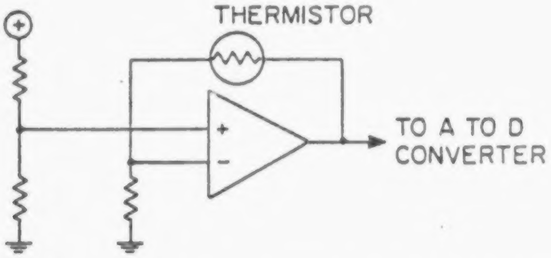

THERMISTOR
+
−
TO A TO D
CONVERTER

Figure 31. CONSTANT TEMPERATURE DETECTOR.

resistance equals the reference resistance. This keeps the thermistor at constant temperature, since temperature is a function of resistance over an appropriate range. The output signal is just the output voltage of the amplifier. It was found that under certain flow conditions this circuit tended to be unstable, undoubtedly since the extremely small thermistor does not act exactly like a resistive element. Such unstable performance is unsatisfactory, but may not recur when the alternate geometry of the replaceable detector configuration is used.

Power supply noise and variations must be considered in selecting an amplifier configuration. In both the constant current and constant temperature modes, the supply is used in the reference network, and therefore must be stable and low noise. In the constant voltage system, the power supply feeds both arms of the bridge and thus power supply variations are minimized. A change in supply voltage will, however, change the operating point of the thermistor and thus change the bridge voltage, but this is a much smaller effect than the direct amplification of the variations in the other systems. The amplifiers themselves are relatively immune to power supply variations. A typical high quality operation amplifier, the Fairchild μA725, has a power supply rejection ratio of less than 5.0 μV/V.

Any amplifier circuit must be able to handle the large dynamic range of signals at the thermistor. The smallest signals are in the few microvolt range, corresponding to ppm size peaks, while air peaks can be on the order of a volt at the detector. While this looks like a 10^6 dynamic range, it is not necessarily that great, since there are no contaminant gases in the scope of this analyzer which approach the 1% concentration level. If a 10 bit analog to digital converter is used which has a dynamic range of 10^3, simple analog switching between the output of the amplifier and the detector should be sufficient to handle the air peaks and the contaminant peaks. It would be best not to have to change the gain of the amplifier itself during the analysis, since the zeroing and drift calculations would not necessarily exactly scale. At lower gains, the zero is less critical, but minimizing perturbations of the amplifier would be preferable for reasons of stability.

The gain of the amplifier would most likely be set at 1000. This would increase microvolt signals to millivolts, which is about the minimum resolution of 10 bit A to D converters, while the largest contaminant peak would be at about 1 volt level at the amplifier output. A gain of 1000 is relatively easy to control, especially at the low bandwidth of this system. The μA725A has a guaranteed minimum large signal voltage gain of 10^6 so at a gain of 1000 the low frequency gain error is about 0.5%.

3.4.2 Drift and Auto-Zero Circuits

Power constraints limit the miniature GC system to operation at room temperature. Room temperature can be expected to change substantially during the day, especially when the thermistor detector is sensitive to changes of microdegrees. Thus some system to handle drift is necessary. It is possible to completely compensate for drift numerically in the roprocessor, provided the input amplifier has unlimited dynamic range. low power supply voltage limits the amplifier output excursion to ut 4 volts peak to peak. Therefore a change of 4 mV at the detector ll be sufficient to saturate the amplifier. A 4-mV signal is large for eak, representing about 3000 ppm in the present configuration, but is ll compared to amplifier drift due to temperature changes.

systems are possible to correct for this drift problem. They both volve correcting one arm of the sensing bridge until the bridge becomes lanced. This automatic zeroing would take place before each sampling. addition, the computer would be able to correct for small offsets merically and also correct for a small baseline drift during the sampling me. Since the sampling period is less than 30 seconds, it is not thought at additional amplifier zeroing would be necessary during that time, at is, that drift over 30 seconds would be within the dynamic range of e amplifier. It would, of course, be possible to rezero the amplifier ring the separation at a time when no peaks are expected. This, however, es not seem to be necessary but may depend upon the insulation capabilies of the final small package.

e automatic zeroing system utilizes a digital to analog converter to ovide a stable variable voltage source, as shown in Figure 32. This ltage source is divided by a resistor network and fed to the side of e bridge opposite to the detector. In this system the computer handles e majority of the zeroing function, since it has to look at the output the amplifier to detect nonzeroed output and to feed the digital to alog converter to correct for that condition. It will be noted that ere is not infinite resolution available with a digital to analog conrter, so the amplifier will never be exactly zeroed. These small igitizing errors can be handled numerically. This system has two main dvantages. First, the computer knows what the offset correction voltage s, since it is controlling the D to A converter. This number might ell be used as a measure of ambient temperature, which is needed to

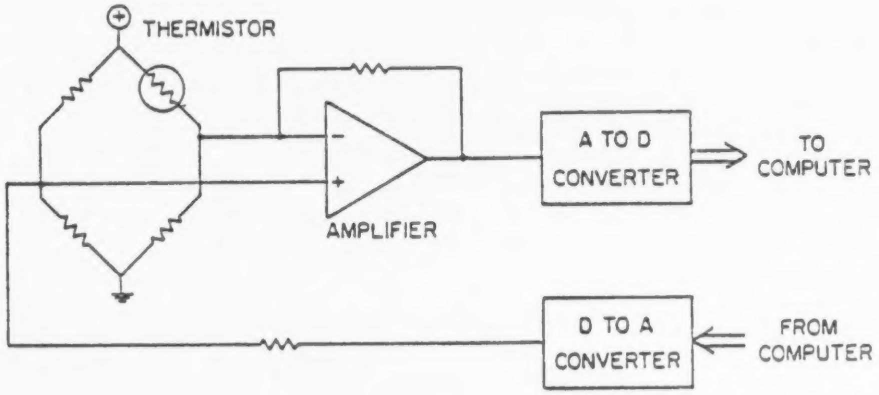


Figure 32. DIGITAL AUTO-ZERO CIRCUIT.

correct for peak retention times during the analysis. Second, the D to A converter's output tracks changes in the power supply voltage which is also feeding the bridge. Thus if the power supply tends to drift during the separation, the bridge would tend to remain in balance more than if the correction signal was applied independently. Also, the D to A converter essentially does not drift, which simplifies matters.

The second, more analog, system is shown in Figure 33. Here an integrator corrects for offset voltage when the analog switch is closed. This system does not have resolution problems, since the output of the integrator can take essentially any value. The main problems involve drift and noise. The drift is associated with input current requirements of the integrator operational amplifier. With a JFET or MOSFET input operational amplifier, such as the RCA CA 3160, the input currents are on the order of 2 pA. With a 1-μF integrating capacitor, this corresponds to a drift of 20 μV over 10 seconds. That is very easy for the microcomputer to deal with numerically. Noise is not likely to be a problem since it is essentially filtered by the large value integrating capacitor.

Both systems appear feasible, but the optimum for a battery powered device would best be determined by experimentation.

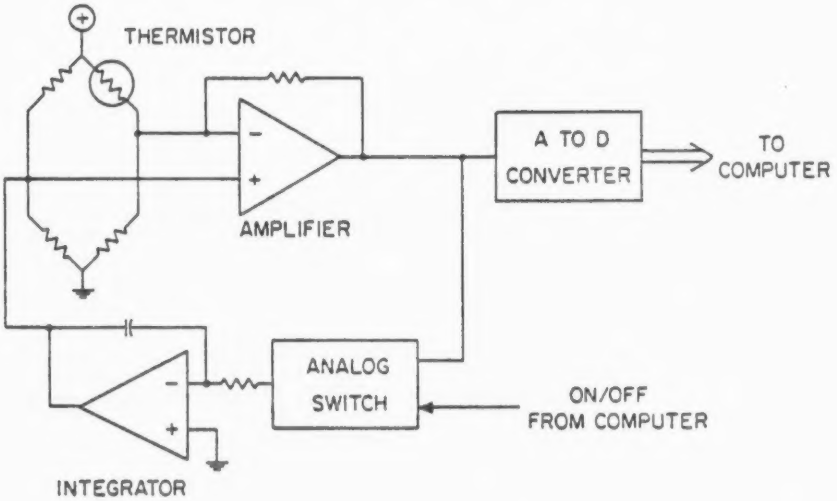


Figure 33. ANALOG AUTO-ZERO CIRCUIT.

3.4.3 Analog to Digital Conversion

The amplified detector output must be converted to a digital signal before processing by the computer. There are a number of ways to perform this operation; the most likely are listed below.

1) Computer-based successive approximation,
2) Successive approximation with external logic,
3) Voltage to period conversion with counting, and
4) External monolithic conversion.

The optimum solution involves trading off speed, power, complexity and resolution. In general, a dynamic range of 10^3 is the minimum necessary which corresponds to 10 bit binary conversion. Since there is likely to be only a single supply voltage available, a number of the more sophisticated commercial devices must be eliminated. There is a strong tend in industry toward the development of high accuracy monolithic converters, so it is likely that advances will be available shortly which can be utilized in future modifications.

Computer based successive approximation is shown in Figure 34. Here the microprocessor handles the approximation routine which requires some 250 µsec for a 2 MHz microprocessor clock frequency. For the highest slew rate likely from the amplifier output, 20 mV/sec, there is a digitizing error possible in this scheme of 5 mV or about 0.5%. This should not be important in this system. The computing time is substantial and during this time the microprocessor must be working solely on the conversion process.

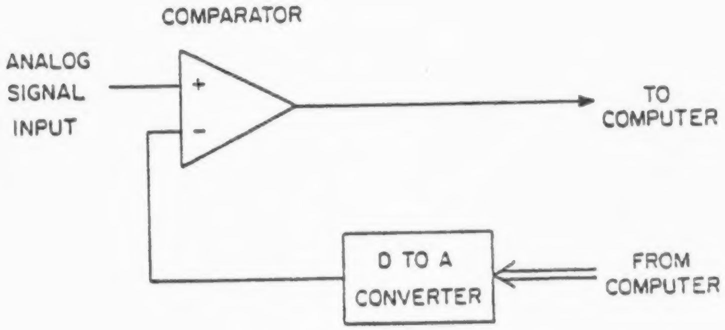


Figure 34. COMPUTER-BASED SUCCESSIVE APPROXIMATION ANALOG TO DIGITAL CONVERSION.

The successive approximation scheme can be dramatically speeded through the use of a dedicated successive approximation register, as shown in Figure 35. Here the conversion time is reduced by almost two orders of magnitude at the expense of an additional device and power.

Another simple conversion process is the voltage to period method. Here a voltage ramp is generated, and the time required to reach the unknown

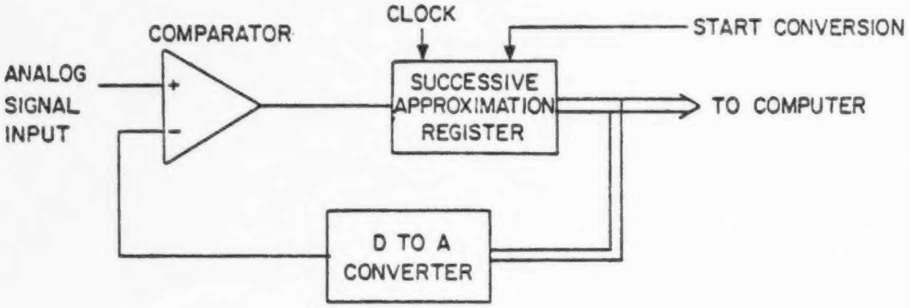

COMPARATOR
CLOCK
START CONVERSION
ANALOG
SIGNAL
INPUT
+
−
SUCCESSIVE
APPROXIMATION
REGISTER
TO COMPUTER
D TO A
CONVERTER

Figure 35. HARDWARE-BASED SUCCESSIVE APPROXIMATION ANALOG TO DIGITAL CONVERSION.

voltage is the measure of the unknown voltage. This can be as simple as shown in Figure 36. If the computer counts, the process is too slow, but external counters can easily be utilized as shown in Figure 37. The external counters essentially do not add to the power requirements, since they only draw power during the conversion process.

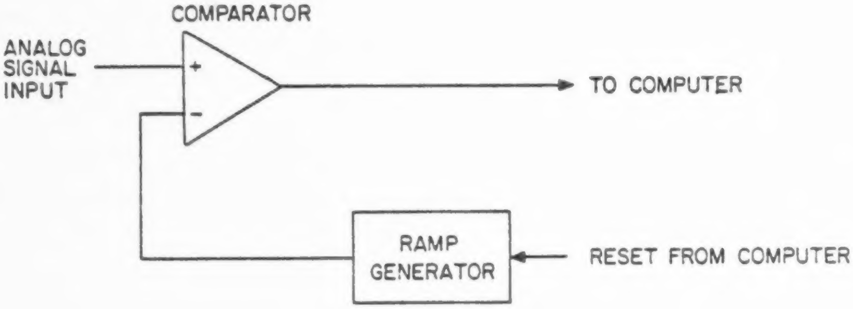

COMPARATOR
ANALOG
SIGNAL
INPUT
+
−
TO COMPUTER
RAMP
GENERATOR
RESET FROM COMPUTER

Figure 36. VOLTAGE TO PERIOD CONVERSION WITH COMPUTER COUNTING.

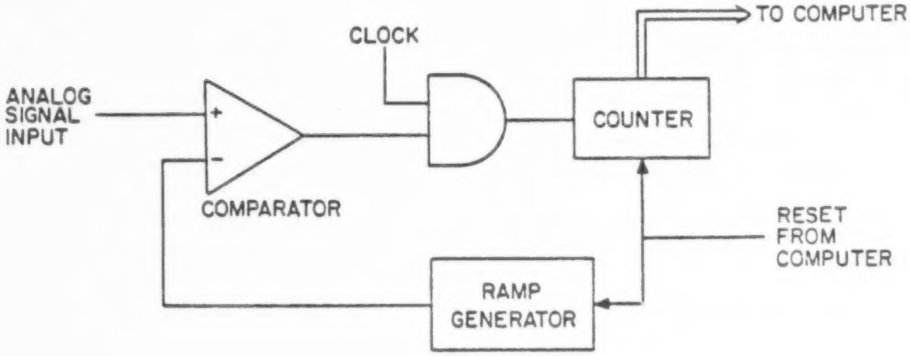

TO COMPUTER
CLOCK
ANALOG
SIGNAL
INPUT
+
−
COUNTER
COMPARATOR
RESET
FROM
COMPUTER
RAMP
GENERATOR

Figure 37. VOLTAGE TO PERIOD CONVERSION WITH EXTERNAL COUNTER.

There are a number of monolithic IC converters on the market which could possibly be utilized, but most are not designed for battery operation and require multiple supplies. An interesting class of converters is being designed for telephone applications which digitally compress the analog voltage.

An example is the MN5100 manufactured by Micro Networks. Here a dynamic range of 72 dB is compressed to 8 bits of digital information, with highest resolution around 0 volts. This particular system is not applicable to the pocket-sized GC system due to power requirements, but future advances in this field may be applicable.

The two systems which appear most feasible are the successive approximation with computer control and the voltage to period conversion with external counter. Both offer good performance at low power and acceptable speed. A choice between the two can only be made after the results of detector modification are known. If the output peak width is reduced as anticipated, the computer-based successive approximation method may be too slow.

3.4.4 Microcomputer

There are two main components that allow a miniaturized gas chromatograph system to be produced. The first is, of course, the miniaturized chromatograph itself; but from a systems point of view, the associated control and processing hardware is just as important, since without the miniaturized electronics the chromatograph would remain a small and fast laboratory instrument.

The microcomputer expands the utility of the miniature GC from a gas separator to a device capable of the analysis of the local environment. It functions both as the system controller or coordinator and as the numerical processor of the detector data. It has only been in the past year that miniature electronic systems of sufficient sophistication to handle a problem of the complexity of the miniature gas chromatograph have become available.

Introduction to Microcomputers--
Microcomputer systems were developed to fill a need for standardized digital components which could be configured to perform a particular system requirement. Prior to their introduction, small to moderate digital systems were of inordinate size and complexity, especially for portable units. Microcomputers offer an alternative by making available the computational power of large computing systems to low cost systems.

Essentially any digital computer system, including microcomputers, are composed of the following parts:

1) Central processing unit (CPU)

2) Program memory

3) Data memory

4) Input/output (I/O) system.

The central processor unit is responsible for handling numerical operations such as addition and for controlling the sequence of such operations. The program memory contains the instructions which describe in detail what operations the CPU is to perform. The data memory contains the input data and the results of the numerical operations, and the I/O system provides a means for both transferring program and data information into the system and for having the system perform a useful function by utilizing the results of its calculations.

The proposed prototype utilizes a microcomputer manufactured by the Intel Corporation and designated the 8748. This is a so-called 8-bit machine. That is, the typical piece of information which is dealt with is 8 binary digits long. This particular device combines the four main parts mentioned above onto a single silicon chip. This provides for a substantially more compact system than was previously possible. A complete description can be found in the Intel MCS-48 Manual [31], but briefly it includes the following parts:

1) 8-bit CPU

2) 1048 x 8 bit electrically alterable program memory

3) 64 x 8 bit data memory

4) 8-bit counter/timer

5) Three 8-bit I/O ports

6) Interrupt capability

This particular unit is well suited for initial prototype development, but is not adequate for the final hand held units, mainly due to power considerations. There are alternate processing technologies becoming popular which should result in lower power alternatives to the 8748. It is expected that these units will become available in the next one to two years. It is important to note that the development effort required for utilization of the 8748 system should be almost entirely applicable to any microcomputer system which becomes more attractive from a power standpoint.

Microcomputer System Software--
It seems most appropriate for this particular system to outline the functions which it is to perform before discussing the hardware required to handle these functions. A microcomputer is most useful in applications such as the miniaturized gas chromatograph where the required functions can be performed sequentially, since the CPU can deal with only one set of information at a time. A simplified flow chart is shown in Figure 38. Some details have been left out for the sake of clarity, but the general control and information flow is readily apparent.

Following down the flow chart, the data collection and analysis proceeds as follows. An external timer produces a signal once each minute which

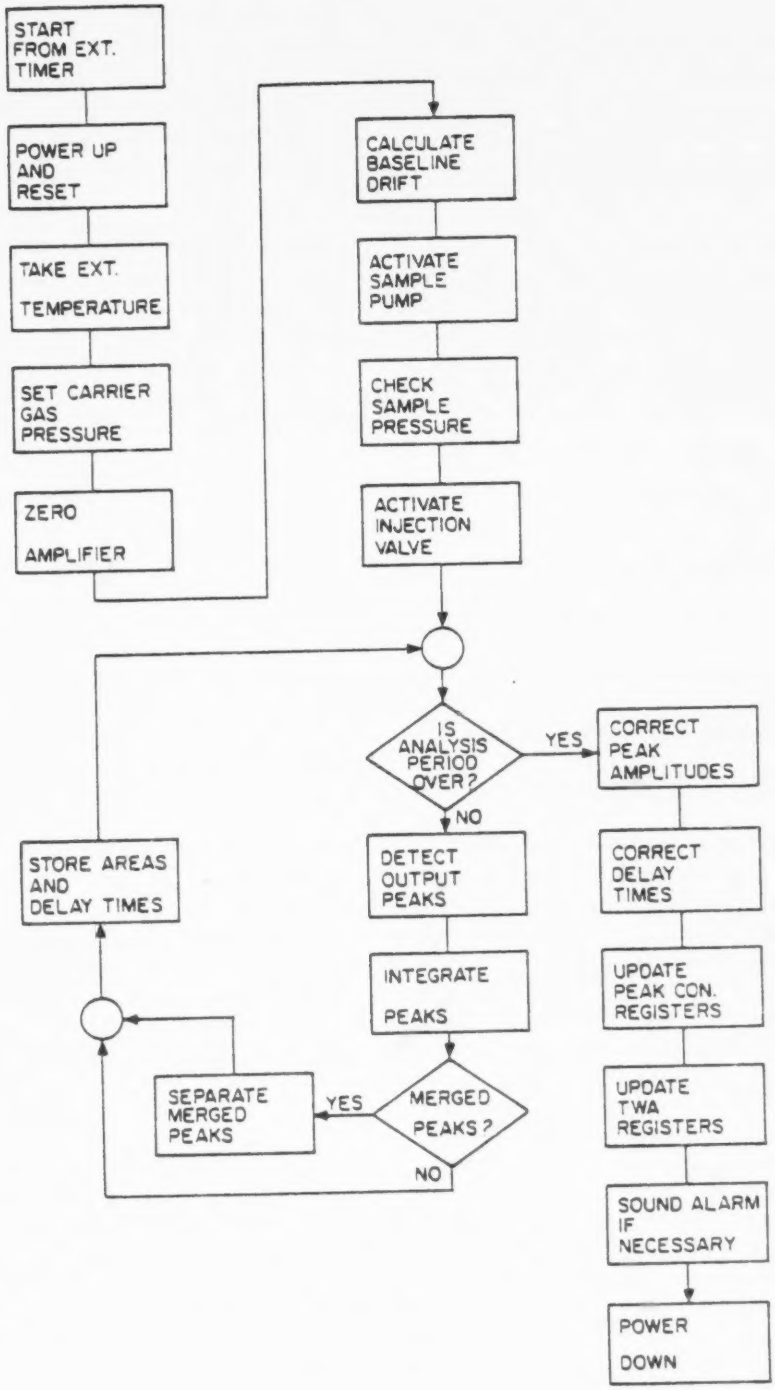

START FROM EXT. TIMER
POWER UP AND RESET
TAKE EXT. TEMPERATURE
SET CARRIER GAS PRESSURE
ZERO AMPLIFIER
CALCULATE BASELINE DRIFT
ACTIVATE SAMPLE PUMP
CHECK SAMPLE PRESSURE
ACTIVATE INJECTION VALVE
IS ANALYSIS PERIOD OVER?
YES
NO
CORRECT PEAK AMPLITUDES
CORRECT DELAY TIMES
UPDATE PEAK CON. REGISTERS
UPDATE TWA REGISTERS
SOUND ALARM IF NECESSARY
POWER DOWN
DETECT OUTPUT PEAKS
INTEGRATE PEAKS
MERGED PEAKS?
YES
NO
SEPARATE MERGED PEAKS
STORE AREAS AND DELAY TIMES

Figure 38. FLOW CHART OF MICROCOMPUTER PROGRAM.

starts the sampling sequence. The microcomputer is turned off between samples to save power, so this timer signal activates an external power-up circuit which both applies power to the microcomputer chip and initializes an internal reset routine.

A number of preliminary details must be taken care of before actual separation can take place. The ambient temperature is measured to be used later to correct peak delay times, the carrier gas pressure regulator circuit is activated to increase the pressure in the surge cavity to the desired level, and the detector amplifier auto-zero circuit is activated to take care of small offsets due to temperature or power supply drift. There is likely to be a small amplifier baseline drift due to temperature changes, so this drift is measured to be used later for peak area correction. The sample pump servo circuit is activated which starts the sample pumping sequence. When the sample pressure reaches the desired level, the sample injection valve is activated and the sample pump is turned off.

The machine now starts the main data collection and analysis portion. The start of an output peak is detected and numerical integration of the peak area takes place. If a double peak is detected it is numerically separated and the individual areas are stored along with the peak retention times. When the analysis period is completed, the retention times are corrected for temperature and checked against the stored list of retention times to determine if the peaks correspond to contaminants which are to be measured. If so, the appropriate concentration registers are checked and updated. If any of the concentrations exceeds a predetermined value, the alarm is sounded to alert the wearer to the presence of a potentially dangerous situation. The computer is then powered down until the next sampling period is to take place.

The display portion of the software is separate from the data analysis program since the display and analysis functions are completely separate. The 8748 is not sophisticated enough to handle a display request and a sampling sequence simultaneously, so a priority must be established. Since the display requests are assumed to take place rather sporadically, the display will probably be given priority. When a key is depressed, the computer is powered up and an external interrupt starts the display routine. The keyboard request selects the gas to be displayed along with the type of concentration desired. The particular concentration is converted from binary to decimal and displayed for a short period of time. The machine is then powered down.

There are some programming details which are important which are not apparent from the flow chart. The major of these involves the use of an 8-bit microcomputer. Eight binary bits represent 256 possible decimal numbers. Since there are about 500 sampling periods in a day, and each sampling involves measurements with about 1000 decimal digit resolution, the total amount of data which needs to be stored is substantially larger than can be handled in units of one 8-bit word. Thus double precision storage of peak areas will be necessary, and the TWA concentration may require triple precision. Since ten gases are to be calculated, with peak, current,and TWA concentrations,some 70 8-bit registers will be necessary simply for data storage. The 8748 has only 64 internal 8-bit registers, some of which are needed during calculations, and the information in these registers is lost during power-down periods, so external CMOS random access memory will be used for data storage. When in the idle state, these memories draw about 15 μA each, and two such memories will be needed.

Portions of the software necessary to implement the flow chart have been written and run on a Z80 microprocessor system, a similar 8-bit machine. It appears that the entire program for the miniature GC system can be implemented using the 1024 words of program memory incorporated in the 8748 chip. Thus no external program memory will probably be necessary, but this will only be known when the entire software package is written and tested. The portions running on the Z80 microcomputer can be used on the 8748 with relatively minor modifications. The larger machines such as the Z80 or 8080 systems are available with monitor programs which allow easy program modification during the prototype stage, and thus are more desirable to use during system development. In addition, assembly language programs can be used which allow the use of timesaving programming constructs during the program development stage.

Microcomputer System Hardware--
The block diagram of the proposed hardware system is shown in Figure 39. This is only one of the many configurations which are possible using the 8748, but is representative of one of the more efficient methods. Essentially the only constraint is in the way the three 8-bit I/O ports are utilized. In this configuration port 0 is used strictly for 8748 to data memory transfers, port 1 is reserved for information transfer between data collection and display portions, and port 2 is used for control of the external hardware. Relatively little I/O expansion has been used in this design which is efficient from a power and chip count basis, and there is room for design changes.

Although most of the hardware subsystems have been discussed in other parts of this report, a brief review of their function is appropriate as related to microcomputer system operation.

The major portions of the electronics system, other than the microprocessor are:

1) Data collection

2) Display and keyboard

3) External data memory

4) Valve and servo control

5) Microcomputer support and control

The data collection system consists of the column output detector, ambient temperature detector, input sample pressure sensor, amplifier, analog multiplexer, A to D converter, and digital multiplexer. For the purposes

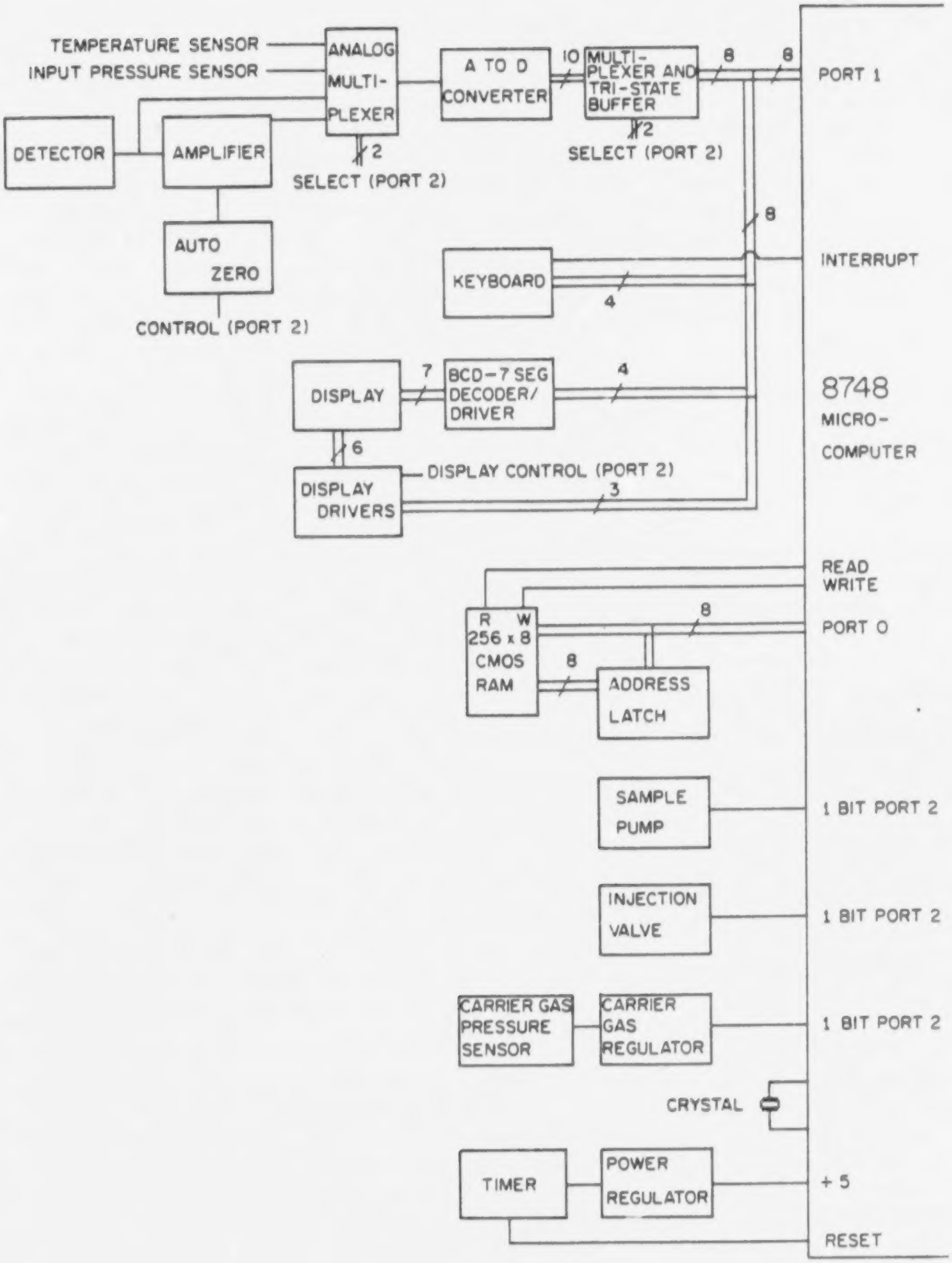

TEMPERATURE SENSOR
INPUT PRESSURE SENSOR
ANALOG MULTI-PLEXER
A TO D CONVERTER
10
MULTI-PLEXER AND TRI-STATE BUFFER
8
8
PORT 1
DETECTOR
AMPLIFIER
2
SELECT (PORT 2)
2
SELECT (PORT 2)
AUTO ZERO
CONTROL (PORT 2)
8
KEYBOARD
4
INTERRUPT
DISPLAY
7
BCD-7 SEG DECODER/ DRIVER
4
8748 MICRO-COMPUTER
6
DISPLAY DRIVERS
DISPLAY CONTROL (PORT 2)
3
READ
WRITE
R W
256 x 8 CMOS RAM
8
PORT 0
8
ADDRESS LATCH
SAMPLE PUMP
1 BIT PORT 2
INJECTION VALVE
1 BIT PORT 2
CARRIER GAS PRESSURE SENSOR
CARRIER GAS REGULATOR
1 BIT PORT 2
CRYSTAL
TIMER
POWER REGULATOR
+5
RESET

Figure 39. BLOCK DIAGRAM OF THE MICROCOMPUTER ELECTRONICS.

of this description, it is assumed that the integrating auto-zero circuit and the voltage to period A to D converter with external counter are used. Since the A to D converter is capable of converting essentially any analog signal to digital form, it is used to give the microcomputer the ambient temperature and sample input pressure along with the data from the detector by using a standard CMOS analog switch. The converter can look at the detector output signal directly, which is necessary for accurate integration of the air peak. The magnitude of the integrated air peak is used to measure the amount of injected sample and to correct the output peaks, so that accurate calibration of the sample injector is not necessary. The microcomputer can also change the amount of time for which the sample injection valve is opened if the air peak becomes too small or too large. This can take care of possible long term drift problems associated with valve wear.

The D to A converter has a higher dynamic range than the 8-bit port. It appears that a 10-bit converter is quite feasible, and 11 bits may also be possible. A digital multiplexer is used here both to switch the 10 bits onto the 8-bit line and to decouple the counter outputs from the I/O lines when these lines are used for display.

The display is envisioned to be a small number of seven segment LED displays, similar to those found in pocket calculators. One digit would be used to show the identification number of the gas being displayed, while the rest would show the concentration of that gas. That concentration could be either in ppm or in percentage of the maximum allowable concentration, depending upon which is thought to be most appropriate. Since most concentration exposure limits specify both peak and TWA limits, both concentrations would be stored by the machine. In addition, the most current concentration could also be displayed to help in tracking down the source of a contaminant. The keyboard would be used to specify the gas wanted for display and the type of concentration desired. A keyboard request would generate an interrupt signal to alert the microprocessor, and the same lines from port 1 would be shared by the keyboard. This sharing is possible since the data collection, keyboard, and display functions can be arranged to be noncoincidental.

The external memory chips are standard devices used here in a quite standard way. The latch circuit is needed to store the memory address during the time that the data itself is on the bus.

The lines from port 2 control the operation of the column and the data acquisition system. The control structure is simplified somewhat by the fact that a number of operations can take place simultaneously and can be controlled with one signal. These operations are the detector amplifier auto-zero circuit, the carrier gas pressure regulating circuit, and the sample pump servo driver system. In addition, since the display function and data acquisition function are mutually exclusive, one line can be used to control both. Since a number of other lines are similarly exclusive, the analog multiplexer lines could be used during the display portion but this is not necessary with the present system complexity. If additional features are found to be desirable, this type of I/O expansion could be used.

The entire electronics package must fit in a rectangular volume about 3 cm by 2 cm by 15 cm. To fit this amount of electronics in such a volume, advanced packaging methods must be used. The lowest volume approach is through the use of custom integrated circuits such as are used in pocket calculators, however, the more limited production runs involved here make that approach not economically feasible. A variant on the custom integrated circuit technique is to use a nondedicated integrated circuit such as Stanford University's KITCHIP. This chip contains about 250 resistors and transistors which can be configured as a vast number of different digital and micropower linear circuits by using a custom metal mask. Such circuits would be valuable in the interface circuitry of the miniature GC to save power and space. The best construction technique for the miniature GC is through the use of hybrid packaging. Here integrated circuits are used in their chip form. Even the largest integrated circuits are only about 3 mm on a side, so very compact circuits can be made by wire bonding the individual chips to metal lines which are on a ceramic substrate. Additionally, miniature chip resistors and capacitors can also be attached to the substrate to further reduce volume. It is unlikely, however, that the microcomputer will be available in chip form since such devices are heavily tested, and the testing is easier for the manufacturers after the device is packaged. Enough of the other devices in the interface section are available as chips to make the hybrid assembly technique useful as a space saving procedure.

Conclusion--
The system electronics are very sophisticated considering the size of the final instrument. These size and power constraints are difficult to deal with, but more and more complex, low power devices are becoming available which should allow the electronics to handle the combined tasks of control, data collection and analysis.

3.5 PRESSURE REGULATOR

The function of the pressure regulator in the miniature GC system is to supply the capillary column with a constant and controlled flow of helium carrier gas. The regulator will be required to reduce the helium pressure from approximately 35 kg/cm^2 (500 psi) in the gas cylinder to a range of 0.07 to 2.1 kg/cm^2 (1 to 30 psi) typical of the operating pressures of the miniature columns.

In the very high precision laboratory chromatographs, the carrier gas flow rate is maintained either by using a mass flow controller on the helium input line or by maintaining a constant pressure differential between the input and output of the column. For typical GC applications it is sufficient to control the carrier flow by venting the column output to atmosphere and controlling the input pressure with a standard 2-stage regulator referenced to atmospheric pressure. Goedert and Guiochon [32] have shown that such a control scheme can lead to quantitative errors in GC analysis (2.5% error when input pressure varies 1%) however, such errors are small compared to the desired accuracy of the pocket-sized GC.

The single most stringent requirement for the pressure regulator in the miniature system is that it be small enough to fit in the pocket-sized instrument. None of the commercial regulators that we could find were small enough to fit into the 6 cm x 6 cm x 2 cm space allocated to the regulator. We have therefore investigated the feasibility of realizing a very small volume regulator utilizing the miniature silicon valves and etched gas channels. The design of such a miniature regulator and a theoretical evaluation of its performance are detailed in the following subsections.

3.5.1 Regulator Design and Fabrication

A very simple, electrically controlled miniature pressure regulator can be realized as shown schematically in Figure 40. The regulator consists of a miniature silicon valve, a surge tank, an IC pressure sensor, and a network of high resistance gas channels. The valve is electronically controlled by the pressure sensor such that it opens when the pressure in the surge tank reaches a predetermined minimum threshold value and closes when a maximum threshold is reached. The resistance gas paths serve to limit the maximum gas flow between the high pressure tank and the surge tank. Since this system is not a high flow general purpose regulator, the size of the resistive paths can be optimized for use with specific column flow rates and input pressures. The volume of the surge tank can be chosen to optimize the duty cycle of the miniature valve.

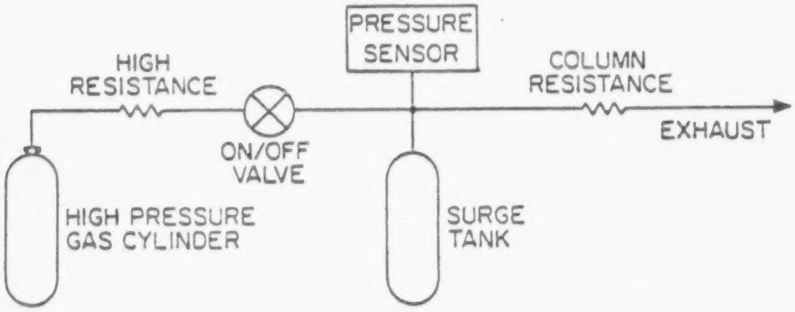


Figure 40. PRESSURE REGULATOR SCHEMATIC.

Figure 41 is a scale drawing of one possible configuration of a miniature pressure regulator, helium tank, and surge tank. The supporting structure is an aluminum block with machined holes for the gas ports. A glass/silicon structure with etched gas capillaries and ON/OFF valve seat is aligned to the feedthrough holes and epoxied to the aluminum block. The IC pressure sensor is cemented to the silicon substrate.

The pressure sensor consists of a thin silicon diaphragm mounted on a 0.5-mm thick piece of Pyrex glass. Four strain-sensitive resistors are integrated on the diaphragm in a Wheatstone bridge configuration. With one side of the silicon diaphragm vented to atmosphere, the diaphragm is deflected by the force of the regulator output pressure, resulting in an

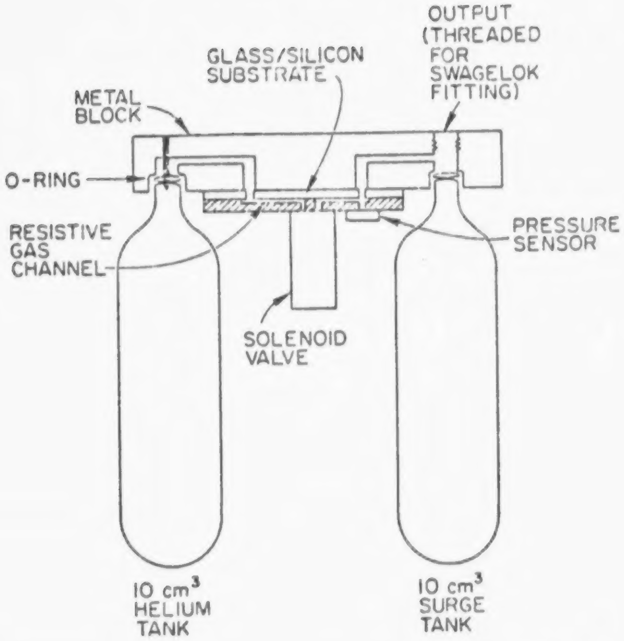

OUTPUT (THREADED FOR SWAGELOK FITTING)
GLASS/SILICON SUBSTRATE
METAL BLOCK
O-RING
RESISTIVE GAS CHANNEL
PRESSURE SENSOR
SOLENOID VALVE
10 cm³ HELIUM TANK
10 cm³ SURGE TANK

Figure 41. CROSS SECTION OF PRESSURE REGULATOR.

output signal from the bridge circuit. Pressure sensors of this type are fabricated at Stanford University and are capable of detecting pressure charges of 0.1 mm of mercury. The output of this sensor can be amplified and used in a dual threshold circuit to activate the miniature valve.

3.5.2 Regulator Operation

The operating characteristics of the proposed miniature regulator and capillary column can be modeled using the electrical analogy of flow resistors and capacitors. This electrical circuit model is presented in Figure 42. R_c and R_l are the channel resistances of the capillary column and resistive gas paths respectively while C equals the capacitance of the surge tank. The values of the resistive elements can be determined from the equation for mass flow in a channel as a function of input and output pressures;

$$F = \dot{V}_o P_o = \frac{Z^2 (P_i^2 - P_o^2)}{24\ \eta L P_o} \quad \rho_o A$$

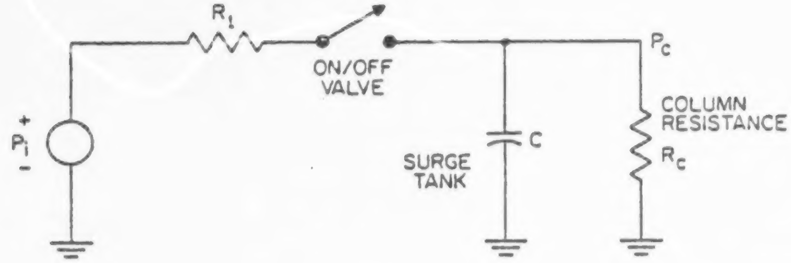


Figure 42. ELECTRICAL MODEL OF PRESSURE REGULATOR.

where

L = channel length

A = the cross-sectional area of the rectangular channel

Z = depth of etched gas channel

η = viscosity of the carrier gas

ρ_0 = density of carrier gas at column output

$\dot{V}_0$ = volumetric flow rate at column output

The resistances are then determined from

$$R = \left.\frac{dP}{dF}\right|_{P = P_i}$$

and are linearized at the operating pressure of the channel input. Thus, given a desired column pressure P_c and a helium tank pressure P_i, the resistors are

$$R_c = \frac{12\eta\, L_c P_0}{Z_c^2 \rho_0 A_c P_c}$$

A_c = cross section of column channel

L_c = length of column

Z_c = depth of column channel

$$R_1 = \frac{12\eta\, L_1 P_0}{Z_1^2 \rho_0 A_1 P_i}$$

A_1 = cross section of resistor channel

L_1 = length of resistor channel

Z_1 = depth of resistor channel

The capacitance is given by

$$C = \frac{V\rho_o}{P_o}$$

where V is the volume of the surge tank.

From the electrical model, two time constants can be derived which characterize the operation of the pressure regulator: the discharge time constant, τ_d, occurring when the valve is closed and the column is bleeding off gas from the surge tank, and the charging time constant, τ_c, occurring when the valve opens and the surge tank fills.

These time constants are given by

$$\tau_d = R_c C$$

and

$$\tau_c = \frac{R_1 R_c}{R_1 + R_c} C$$

The charging and discharging pressures about an operating pressure P_c are given by

$$P = (P_c - P_o)\, e^{-t/\tau_d} + P_o \qquad \text{discharging}$$

$$P = (P_c - P_i)\, e^{-t/\tau_c} + P_i \qquad \text{charging}$$

If the regulator's output is required to be within x% of the desired operating pressure, the charge time (valve open) and discharge time (valve closed) are determined from

$$t_d = x\%\ \tau_d \qquad \text{discharge time}$$

$$t_c = x\%\ \tau_c \frac{(P_c - P_o)}{(P_i - P_c)} \qquad \text{charge time}$$

Once the operating pressure and flow rate of the column are determined, the regulator threshold pressures set, and the range of input tank pressures determined, the above equations can be used to design the length and depth of the R_1 resistive gas channel and to determine the cycle time of the miniature valve as it attempts to maintain the output pressure P_c.

As an example of the operation of this pressure regulator system, the design calculations for a 1-m column operating at 1 kg/cm^2 (15 psi) are

esented in Table 5. Allowing a ±0.5% variation in pressure, the dis-
iarge time (time the valve is off per cycle) is 110 seconds, while the
iarging time or valve actuation period varies from 0.6 msec to 218 msec
epending on the pressure in the helium supply tank. Though these valve
tuation times might not be optimum for repeatability and power consump-
ion, they are at least in the range of what is possible using the current
esign of miniature valves.

Table 5. Operating Parameters of a Miniature Pressure Regulator.

olumn Parameters	
Length 100 cm	Input pres. $P_c = 1$ kg/cm^2 (15 psig)
Depth 25 μm	Volumetric flow 0.7 μl/sec
Width 140 μm	Resistance 6.69×10^{12} dyne/g-cm^2
essure Regulator Parameters	
Surge tank 10 cm^3	$R_1 = 1.8 \times 10^{10}$ @ $P_i = 1.5$ kg/cm^2
Input pres. 1.5-35 kg/cm^2	$R_1 = 1.21 \times 10^9$ @ $P_i = 35$ kg/cm^2
egulator Operation	
Output pressure	$P_c = 1$ kg/cm^2
Pressure variation	±0.5%
Charging time	0.6 msec @ $P_i = 35$ kg/cm^2
	218 msec @ $P_i = 1.5$ kg/cm^2
Discharge time	110 seconds

.6 BATTERY POWER SUPPLY

ne battery power supply in the pocket-sized GC will consist of one or
ore rechargeable batteries capable of providing continuous power to the
ystem for eight hours. The size, weight, and number of batteries utilized
ill depend upon the number of supply voltages required by the system and
ne current drain at each voltage. Since the battery unit will most likely
e both the bulkiest and heaviest component in the GC system, it is desir-
ole to minimize both the magnitude and number of supply voltages and the
ower consumption of the unit.

n optimum power configuration, one which we believe is feasible, is to
tilize a single 6-volt supply. The microprocessor and logic circuitry

run on 5 V which can be obtained from the 6-V source with a voltage regulator. The valves can be made to operate at 6 V as can the pressure sensors, display, and amplifiers. The thermal conductivity detector is the only component which might suffer under this low voltage restriction. The detectors that we have fabricated thus far are best operated in the range of twelve to fifteen volts, and reduction to a 6-V supply will reduce their sensitivities by a factor of two. This reduction in sensitivity is a direct tradeoff with decreased package size and weight realized by using only one supply voltage.

There are a wide variety of sealed, rechargeable nickel-cadmium batteries on the market which are designed for use in portable instruments. They are intended for continuous discharge during an eight to ten-hour period and then over-night recharge. The normal life of these batteries is from 300 to 1000 charge-discharge cycles.

The final choice of a battery will, of course, depend upon the physical space available in the instrument and the power consumption of the electronic package. As a design example, the system configuration shown in Figures 1 and 44 utilizes a single 6-V, 750 milliamp-hour (mAh) battery manufactured by Gould (#CS305 NICAD). This cylindrical battery is 2.55 cm in diameter, 11.88 cm long, and weighs approximately 160 grams. It is capable of delivering an average of 93 mA for an eight-hour period before its output voltage drops from 6 to 5 volts.

Once the current and charge limitations of the battery supply have been determined, a power budget can be established for the various electrical components in the instrument. Table 6 lists the estimated current consumption of the system components operating over an eight-hour day. The total current use listed in Table 6 is approximately equal to the 750 mAh available from the single battery, however, the current drawn by the microprocessor is based upon continuous operation. If the GC separation and data analysis can be completed in much less time than the minute sampling interval, then the microprocessor can either be slowed down or powered down during the remaining period and reactivated just before the next sample is to be taken. Such a scheme might cut hundreds of milliamp-hours off of the microprocessor's consumption, and extend the system operating time beyond eight hours.

Provided that the energy consumption of the electrical system can be held below 1 amp-hour at 6 volts, and that only one supply voltage is required, the battery power supply should not prove to be a major obstacle to the development of the pocket GC. There is a sufficient variety of battery geometries and sizes available to fit within the dimensional and weight constraints of the miniature system.

3.7 MECHANICAL CONSIDERATIONS

There are several mechanical problems associated with the fabrication of the pocket-sized instrument which have to be considered. These are:

1) Attachment of input gas tubes to the integrated column

Table 6. Estimated current consumption of system components for 8 hours.

Component	Operation	Consumption (mAh)
Sample valve	Pulsed 1 msec per minute @ 30 mA	0.004
Sample pump	1 sec operation per minute @ 75 mA	10.0
Regulator valve	100 msec operation per minute @ 30 mA	0.4
Pressure sensors	Continuous @ 1 mA each (2 sensors)	16.0
Detector	Continuous @ 6 mA	48.0
Microprocessor	Continuous @ 75 mA*	600.0
Amplifiers	Continuous @ 10 mA	80.0
Custom Interface Circuitry	Continuous @ 3 mA	24.0
		778.0

*This current is an estimate based upon data for an announced Hewlett-Packard 16-bit CMOS microprocessor.

2) Heat sinking the silicon-glass column structure

3) Thermal insulation of the integrated GC package within the instrument

4) Final package configuration and construction.

Though none of these problems is thought to pose a serious obstacle to the realization of the pocket-sized instrument, they are very important parts of the instrument design and are considered here for completeness.

3.7.1 Tube Attachment and Heat Sinking

These two areas, tube attachment and heat sinking, are considered together since they both involve fastening metal structures to the silicon wafer, and most likely will be combined together into a single structure. The method of tube attachment which has been used to date is to simply butt the flattened and polished end of each gas tube against the silicon wafer over its feedthrough hole and epoxy it in place. This method is time consuming and results in a structurally weak joint. It would be advantageous to first secure the tubes to a rigid structure serving to add both mechanical strength and to position the tubes relative to one another. This complete tube structure would then be positioned against the silicon wafer such that all gas ports were aligned simultaneously.

The addition of a heat sink to the miniature GC is necessary since it is desirable to increase the thermal mass of the device. Temperature changes in the silicon wafer caused by power dissipated in the TC detector and by environmental temperature changes result in detector noise, drift, and sensitivity variations. Though it is impossible to maintain a constant column and detector temperature with a heater due to power limitations, the addition of thermal mass to the unit will slow down the temperature variations with time, and will result in small and approximately linear variations during the GC analysis period. The microprocessor can easily compensate for the linear baseline drifts which result from these small, linear temperature drifts.

One possible scheme for combining the heat sink and tube attachment structure is shown in Figure 43. A brass block serves as the thermal mass of the heat sink. Holes drilled through the block line up with the output ports in the silicon wafer, and the input tubes are brazed onto the block. Since the two gas exit ports can be vented directly into the headspace of the instrument, no tubes need be attached to those holes. A thin layer of a Dupont FEP fluorocarbon film is used to attach the brass to the silicon. The FEP film, applied as a sheet between the surfaces, softens at 205°C and bonds the surfaces together when it is recooled. The addition of a brass block on the glass side of the GC structure completes the temperature stabilization assembly. The addition of 150 grams of brass increases the thermal mass of the GC by a factor of 120.

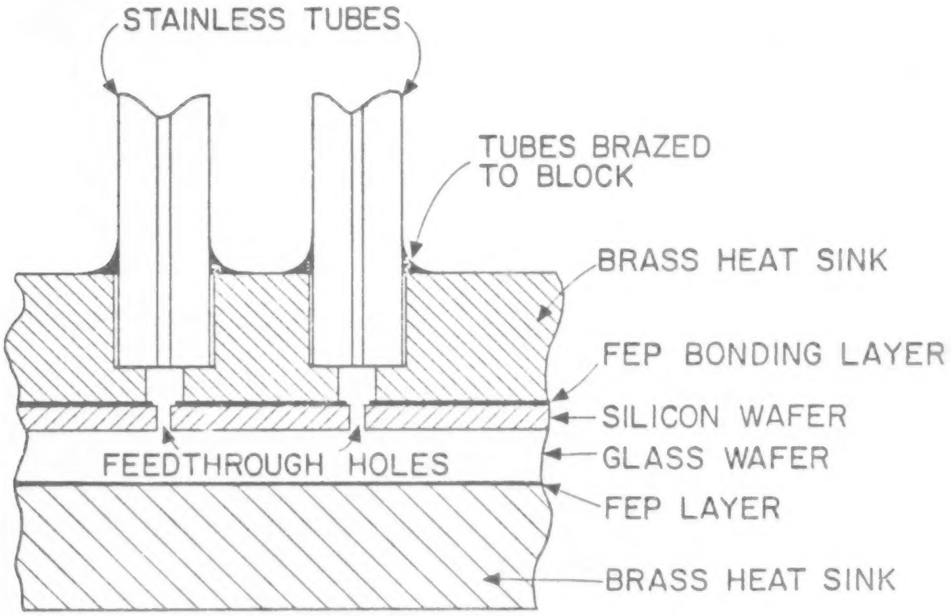


Figure 43. HEAT SINK AND TUBE ATTACHMENT SCHEME.

3.7.2 Thermal Insulation

Since the thermal conductivity detector is sensitive to millidegree temperature variations in the silicon surrounding it, the heat sink is necessary to average out temperature fluctuations, and thermal insulation is required to further reduce the influence of the environmental temperature. Since temperature variations from 0°C to 50°C can be envisioned as a wearer of the instrument walks from outdoors in the winter into a furnace room, the insulation may even be of greater importance than the heat sink. It has been found that elimination of convective air currents around the GC is of primary importance when attempting to reduce thermal noise. It is probable that a molded Styrofoam block or spun fiberglass layer surrounding the heat sink will provide as good an insulating layer as is achievable in the confines of the small package.

3.7.3 Package Configuration and Construction

Two important aspects of the layout of the various components in the pocket-sized package are thermal considerations and user convenience. As has been mentioned previously, the GC package must be well isolated thermally from any heat producing elements. Inside the pocket-sized device, the electronics package is the main offender, dissipating about a half watt of power as heat. The servo and pressure regulator also produce some heat, but most likely not enough to be seen by the detector. It is therefore desirable to locate the GC away from the electronics, preferably in a separate sealed compartment. It is also desirable to use as much space as possible for the GC so that a maximum amount of insulation material can be used.

In terms of user convenience, the package should be laid out such that there is easy access to the battery and helium tank for replacement by the field user, and more difficult access (though not requiring complete disassembly) to the programmable memory chip for reprogramming calibration of the GC. Also for obvious reasons, the controls, display, audible alarm, and sample inlet should be on the "front" of the instrument.

The package configuration sketched in Figure 44 fulfills the above requirements. The GC is in a large sealed compartment by itself for thermal isolation, the battery and helium tank are accessed through a door in the back of the package, while the electronics unit can be serviced through a more secure door on the front side of the device. Though such a configuration may not prove to be optimum, it at least demonstrates the feasibility of including all the necessary components in a 4 cm x 8 cm x 15 cm package. The estimated weight of the instrument, 0.6 kg, is broken down by components in Table 7.

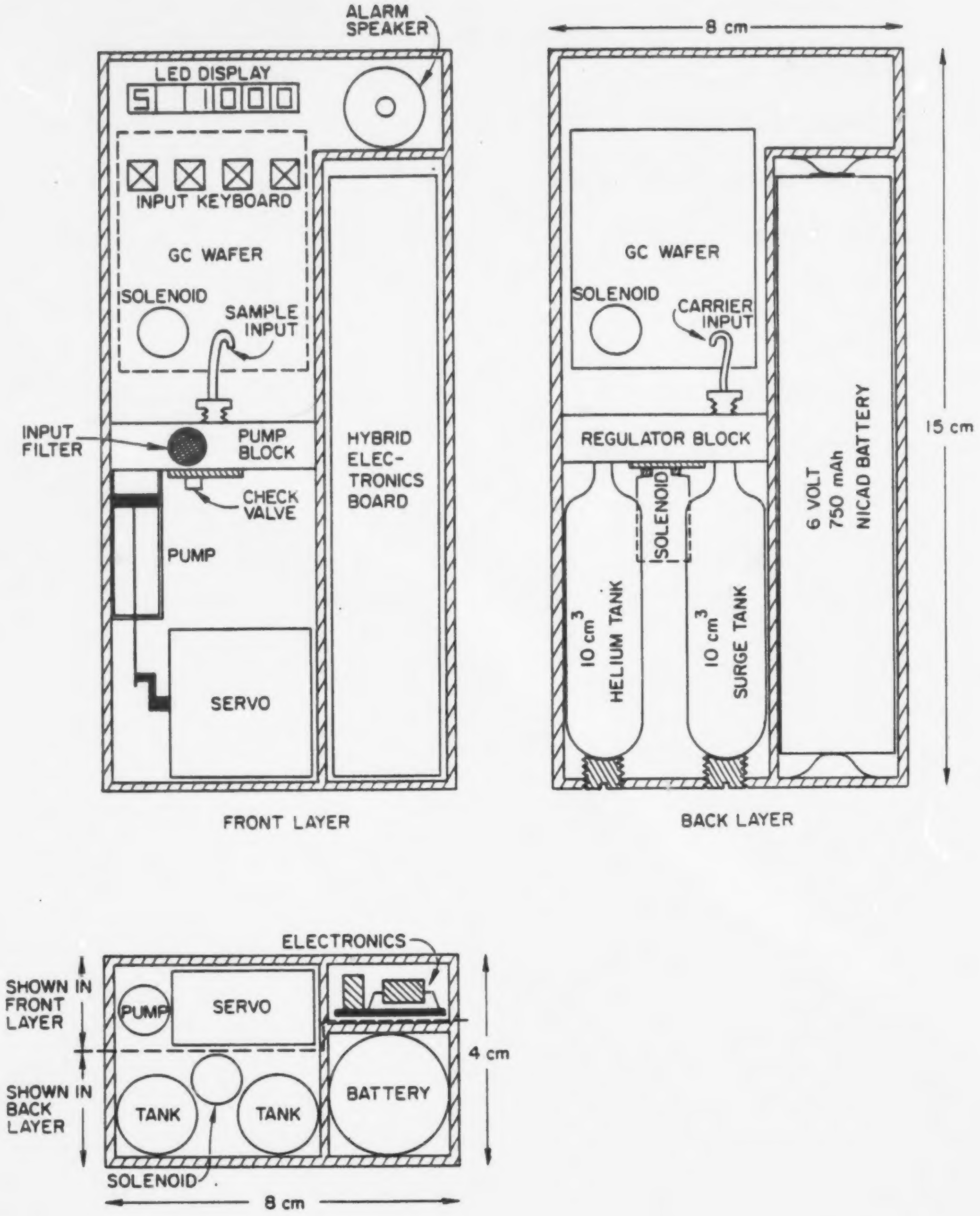

ALARM SPEAKER
LED DISPLAY
5 1000
INPUT KEYBOARD
GC WAFER
SOLENOID
SAMPLE INPUT
INPUT FILTER
PUMP BLOCK
CHECK VALVE
PUMP
SERVO
HYBRID ELEC-TRONICS BOARD
FRONT LAYER
8 cm
GC WAFER
SOLENOID
CARRIER INPUT
REGULATOR BLOCK
SOLENOID
10 cm³ HELIUM TANK
10 cm³ SURGE TANK
6 VOLT 750 mAh NICAD BATTERY
15 cm
BACK LAYER
ELECTRONICS
SHOWN IN FRONT LAYER
SHOWN IN BACK LAYER
PUMP
SERVO
TANK
TANK
BATTERY
SOLENOID
4 cm
8 cm

Figure 44. LAYOUT OF COMPONENTS IN A POCKET-SIZED PACKAGE.

Table 7. Estimated weight of system components.

Component	Mass (g)
Battery	160
Brass heat sink	150
Aluminum regulator block	58
Gas tanks	44
Servo	21
Pump	15
Electronics	60
Switches & LED display	30
Plastic case	60
TOTAL	598

4. FUTURE DEVELOPMENT

It has been shown that it is feasible, using existing silicon etching, integrated circuit, and GC technologies, to produce a pocket-sized personal air contaminant monitor based upon gas chromatographic analysis. There is, however, a significant amount of developmental effort which must be invested in the device before it will be ready for commercialization and available to industry as an off-the-shelf product. The next logical step in the evolution of such a device is the development of a prototype model which can be field tested and evaluated by its potential users. The following subsections describe the developmental effort required on each of the major system components to realize such a prototype model.

4.1 DETECTORS

Since the detector represents the limiting factor in the sensitivity (and detectivity) of the GC system, any improvement in this component will be of direct benefit to the overall system performance. To realize the desired 1 ppm detectivity, the currently utilized thermistor TC detector must be reduced in volume and thermal mass. If commercial bead thermistors are utilized (a logical choice for the next generation of detectors) the dimensions of the detector cavity must be decreased to very closely match those of the thermistor bead. The open channels through which the thermistor's leads exit must also be eliminated. In order to facilitate lining of the column without lining the detector, and to increase the yield of working systems, the complete detector structure must be made removable and replaceable. Such a modification is necessary if high quality GC performance is to be achieved. These detector improvements represent slight variations and advances in the scope of existing fabrication technology. Further detector advances, such as utilization of thick film thermistors or the development of a miniature photoionization detector or other types of detectors represent both significant advances in technology and in detector performance.

4.2 COLUMN LININGS

Continued effort must be directed toward developing new linings and lining techniques for the miniature capillary columns. The broad applicability of the GC analysis technique in general is due to the wide variety of column linings and supports which have been made available over the past twenty years. Application of these linings to the miniature system is necessary to both improve its performance and to broaden the scope of its possible applications.

4.3 INTEGRATED CAPILLARY COLUMN AND VALVES

The techniques for designing and fabricating the integrated capillary column are very well developed at this time. For use in the prototype gas analyzer, the only column modifications necessary are changes in the length, width, and depth of the capillary groove to optimize the GC separations and analysis times achieved by the column.

Likewise, the integrated valve design currently being used is close to being satisfactory for the portable instrument. Improvements such as decreased dead volume, increased solenoid efficiency, and higher-yield diaphragm production are all possible with existing technology and represent easily achieved, though very significant, improvements.

4.4 PRESSURE REGULATOR

The miniature pressure regulator appears to be simple in conception; but since it has not yet been fabricated, potential pitfalls may exist. Realization of the system entails development of a high-pressure miniature valve, pressure sensing and control electronics, and a mechanical scheme for mounting the various component parts of the device. Once again, all of these developmental tasks appear to be well within existing technology.

4.5 SAMPLE INPUT PUMP

This system component is extremely simple to realize and should represent very little developmental effort beyond simply making the device fit into the appropriate volume.

4.6 MICROCOMPUTER AND ELECTRONIC SYSTEMS

Development of the electronics package for data analysis and control of the instrument can be divided into hardware and software functions. The major challenge associated with the hardware design will be trying to meet the very low space and power restrictions imposed by the pocket-sized, battery operated instrument. At present there are no microprocessor or microcomputer IC chips available with sufficiently low power consumption to operate continuously for 8 hours on the amount of power available for the system; however, we are optimistic that such a device will be available in the near future (2 to 3 years). In the meantime, system development can proceed using the higher power Intel 8748 microcomputer device; and if power can be conserved by powering down the 8748 when it is not needed for control or computation functions, it may even prove to be a satisfactory device for the battery powered instrument. In order to fit all of the electronics into the pocket-sized package, hybrid assembly techniques and most likely even custom integrated circuits will be required. Except for the possibility of a new low power IC microprocessor, realization of the computer and interface electronics represents no new technology or devices, but rather a utilization of existing high-technology circuits, devices, and packaging methods.

Software development for the microcomputer will be based upon the computational power of the 8748 and will have to be tailored to the performance and design of the complete GC system as they evolve. We foresee no major obstacles to be overcome in this developmental area.

4.7 PACKAGING

Considerable effort will be required to design and assemble the prototype package for the instrument. Again, size and weight constraints will be of primary importance, but consideration will also have to be given to thermal isolation and insulation aspects of component placement. New techniques will have to be developed for attaching the input tubes and heat sink to the silicon GC wafer and attaching the pressure regulator substrate wafer to the metal tank-mounting block. No new materials or minor components (e.g. switches, LED displays, alarm speaker, etc.) need be developed for the prototype instrument.

4.8 DEVELOPMENT EFFORT

The development of a prototype GC gas monitor described in this report will involve a wide variety of high technology processes such as silicon micromachining, integrated circuit fabrication, hybrid packaging, thermistor fabrication, and Parylene deposition. In addition, support services such as metal machining and chemical analysis will be required. The length of time and the number of man-years of effort involved in realizing the portable prototype system are difficult to estimate since they depend upon the availability of these high technology facilities and personnel.

Based upon our past experience with the development of integrated GC and the availability of the required technology and equipment at Stanford University and in the Stanford Integrated Circuits Laboratory, a rough estimate of prototype development effort is 6 man-years of work spread over two years in time. This estimate is broken down into individual component development times in Table 8. These estimates take into account both the technology involved with realizing each component and the amount of improvement required in component performance beyond what is now available.

Table 8. Estimated Development Effort for Prototype System Components

Component	Effort (man-years)
TC Detector	1
Column Lining	1
Integrated Valves	0.5
Pressure Regulator	0.5
Sample Injection Pump	0.33
Microcomputer Electronics	2
Packaging	0.66
TOTAL	6

5. APPLICATION OF THE POCKET-SIZED GAS ANALYZER.

5.1 CALIBRATION

The miniature GC system can be programmed to detect specific contaminant gases and calibrated to accurately measure their concentrations by simply storing the appropriate information in the microcomputer's memory. There are no zero or full scale adjustments to be made, for these operations are performed digitally. The only calibration information needed by the instrument is the amplitude correction factors and the temperature-corrected peak retention times for each contaminant gas. At present the probable device-to-device variation in peak retention times and amplitudes is not known, nor is exact long term drift data available, so the extent of device calibration can only be speculated. The short term stability of an individual injection system and column is known to be within 1% in both retention time and sample size, which is very favorable. From this short term data it is assumed that frequent calibration will not be necessary, especially to hold the overall 10% system accuracy.

Calibration of the device is similar to the calibration of standard laboratory chromatographs. A known concentration of each of the contaminant gases of interest is injected into the GC system. The output of TC detector is then analyzed for both the retention time and integrated area of each of the resultant output peaks, and each peak is identified with one of the sample contaminant gases. This process is repeated at several elevated temperatures to yield the temperature-corrected peak retention time for each contaminant. This information is then stored in the computer's memory along with the peak amplitude scale factors necessary for the GC system to determine the correct concentrations of each of the sample gases.

At present it is assumed that the calibration and scale values are held in the microcomputer's program memory. In the 8748 the program memory is a type of electronic memory known as EPROM, for electrically programmable read only memory. The data in this type of storage is, for all practical purposes, permanently held, yet changes can be made by first erasing the contents of memory with externally supplied UV light, and then electrically writing the desired information into the blank memory. It would be most convenient if these scale factors were contained in a separate memory chip which could be easily removed from the system and corrected, however it is not yet clear what the final system configuration will be. The separate calibration chip would increase system complexity somewhat which must be traded off against the inconvenience of having the scale factors merged with the program in the microcomputer program memory. In any case, to reprogram the memory chip will require the use of a specialized electronics package which will be supplied separately from the pocket-sized GC. The final complexity, sophistication, and cost of the programming instrument will depend upon whether it is designed to monitor the calibration tests, calculate the scale factors, and program the memory, or simply to insert the user-determined numbers into the memory chip.

If a set of gases is chosen which is of similar interest to people in a number of areas so that production runs of hundreds or thousands of GCs can be made with a particular column lining, then a simplified calibration routine is possible. It is assumed that the major variation between columns will be in the exact amount of stationary phase in each column. If the retention times scale reproducibly with varying thicknesses of lining, and the temperature dependence is understood for the different thicknesses, then only a subset of the gases of interest, perhaps one or two, will need to be tried to completely characterize a particular unit. This simplified calibration procedure would decrease the time needed to test a unit, and offers the possibility of changing the unit to respond to a different gas by consulting a table of relative retention times instead of a more tedious calibration procedure.

As mentioned in section 3.1.4 describing the performance of the GC system, a column supplied with a specific lining may not be optimum, or even satisfactory, for separating certain contaminants of interest. In this case the user will have to use a second pocket-sized GC for those contaminants or will have to re-line the miniature column with a stationary phase appropriate for the separation of the desired compounds. Re-lining the column followed by re-calibration of the instrument should require only rudimentary chemical facilities, but having this capability will greatly enhance the user's ability to monitor a wide variety of contaminants with a single instrument.

5.2 PROJECTED OPERATION

The miniature gas chromatograph is an extremely simple instrument to operate due to the advanced control capabilities of the microcomputer. After overnight recharging, the unit is taken to the work area and attached to the worker and turned on. The start button is pushed which resets the concentration registers and starts the one-minute sampling cycles. The instrument is capable of unattended operation from this point until the end of the day. At the end of the shift the TWA and peak exposures can be read from the display and recorded for each of the 10 different gases. Since this recording is a tedious process, and the chance for error exists, a large operation with a number of analyzers in operation may wish to have an additional piece of electronic equipment which would automatically read the contents of the gas analyzer's memory and record the information in the appropriate worker's file.

An operational advantage which is possible with this computerized gas analyzer is its ability to continuously monitor the exposure to each of the different gases and compare the exposure to the particular limit appropriate for that particular gas. If any of the exposures is exceeded, an alarm will be sounded which will warn the user of a dangerous situation.

After a number of days the He carrier gas supply will be exhausted. If the gas supply runs out during operation, the microcomputer will detect the lack of flow and sound the alarm. The tank changing is essentially the same as either changing a CO_2 cylinder in other miniature gas operated devices, or changing a gas tank of a miniature propane torch. A small amount of air may be introduced into the carrier gas during tank changing. and this air must be purged before the unit is ready for operation. It is thought that this purging cycle would be completed in about an hour.

The battery is capable of being recharged from 300 to 1000 times, and is straightforward to replace after that time. All other portions of the instrument are solid state, and should not require periodic maintenance.

Depending on the final separation ability of the column, it is possible that the instrument will be unable to distinguish between two different gases. It is impossible to guarantee complete separations, but it should be possible to select a column lining which would distinguish the gases known to be found at a certain location. By using different column linings, then, different classes of gases can be analyzed without changing any part of the rest of the instrument.

The inclusion of the microcomputer is the key to simplified operation of this instrument since routine functions such as amplifier zero are performed automatically, and the detector output signal is automatically converted into absolute concentration information. The unattended operation is also necessary and useful for a personal air contaminant meter.

5.3 MARKET

It is useful to determine the extent and needs of the market while an instrument is being designed, so that the appropriate controls and features can be incorporated in the device. The inclusion of the microprocessor makes this slightly less important, since what would have been drastic changes in the electronics section can be handled by simply changing the computer's program memory. These changes can radically alter the configuration and operation of the device, especially how the keyboard and display are controlled.

The miniature gas chromatograph is capable of being used in a wide variety of applications involving the analysis of chemical substances. It is approximately an order of magnitude faster than laboratory instruments at significantly reduced cost. The high speed operation is potentially useful for process control where the chromatograph is the active analysis portion of the feedback system or in patient monitoring in a medical situation where rapid analysis is necessary. Both of these applications involve the detection of substances of known composition but unknown concentration, a useful condition for simplified analysis.

In the toxic gas analysis field, the miniature gas chromatograph is useful in two slightly different areas. The first is as an individual exposure meter, and the second is as a survey instrument.

The exposure meter application requires a very low cost instrument capable of completely automatic operation and minimal maintenance and calibration. The instrument must be capable of operating in temperature extremes, be resistant to breakage, and be unobtrusive to the wearer. At present the miniature chromatograph, at a probable retail price of about $1000, may be too expensive for widespread dosimeter application, especially for the smaller companies which cannot afford large expenditures for safety and health purposes. The present weight of about 0.6 kilograms may prove cumbersome in some environments.

In the first years of production, before economics of scale reduce the retail price, the survey instrument may prove to be more viable. Here the user would be a more sophisticated safety officer who would be able to have most of the capabilities of a laboratory chromatograph in the field. Surveys of locations for the concentrations of a wide variety of gases could be performed quickly and accurately with one or two miniature chromatographs each optimized for a different set of gases through the use of different column linings and computer programs. For such a survey instrument the cost is not a particular constraint due to the more intensive use of the device, and the larger battery weight is not as important. While it is possible to use the personal monitor as a survey instrument, the instrument would likely have a more elaborate keyboard to allow more control over the device operation.

The main advantages of the miniature chromatograph over such devices as chemical indicator tubes should be readily apparent to the users. The instrument has a very low variable cost per sample, due only to the tiny amount of carrier gas and electricity used. Its ability to distinguish a wide variety of hydrocarbons along with analyzing and storing different types of concentrations for each of the gases is substantially more sophisticated than the simple average readings of a group of gases available with indicator tubes, or the meter readings or strip chart records obtainable with photometric or sensitive electrode instruments. In many cases the miniature GC can free laboratory instruments for other laboratory measurements and thus allow a company's chemistry lab to be run more efficiently. The ability of the miniature chromatograph system to audibly warn the user of dangerous environments is unique in the dosimeter area and may represent the most useful advantage of such an instrument.

6. CONCLUSION

It appears feasible to develop a pocket-sized gas analysis system based upon a miniature gas chromatograph and microcomputer which can perform the following functions:

1) Sample the atmosphere automatically for eight hours
2) Measure the concentration of 10 different toxic gases simultaneously to within 10% accuracy
3) Calculate and store the time-weighted average (TWA) and peak concentration for each of the gases
4) Measure concentrations at the 10-ppm level with probable further improvements to the 1-ppm level
5) Be capable of displaying any of the stored concentrations upon demand
6) Sound an alarm when any concentration exceeds a predetermined value.

This instrument would be fully self-contained in an 8 cm x 4 cm x 15 cm package weighing approximately 0.6 kg. It would consist of a miniature integrated gas chromatograph, a sample input pump, a helium carrier gas supply and custom pressure regulator, a microcomputer system, and a rechargeable battery power supply.

The miniature gas chromatograph is the heart of the proposed instrument, performing the actual separations of contaminant gases from the air samples. It consists of a capillary column, a sample injection valve, and a thermal conductivity detector all integrated on a single 5-cm diameter silicon wafer. The capillary column is formed by etching a long spiral groove in the surface of a silicon wafer and capping it with a Pyrex glass cover plate which is hermetically sealed to the silicon. The integrated injection valve is a simple, solenoid actuated diaphragm valve with an etched silicon valve seat and orifice fabricated on the same silicon wafer as the capillary column. The small volume thermal conductivity detector is also housed in an etched silicon structure which is attached directly to the main silicon substrate wafer. All of these structures are fabricated using high technology silicon "micromachining" processes.

A small servo-driven syringe pump serves to draw in the air samples from the environment and pressurize them for injection into the column. The helium carrier gas for the chromatograph is supplied in a replaceable 10-cm^3 gas cartridge. It is reduced in pressure by a miniature regulator system consisting of an integrated silicon valve, a silicon pressure sensor, and a 10-cm^3 surge tank. Both the sample pump and the pressure regulator are under the direct control of the microcomputer.

A state-of-the-art integrated circuit microcomputer is included in the instrument to handle control and data processing functions. The microcomputer, with its associated program memory, data memory, analog to digital converter, detector amplifier, and other display and control circuitry, controls the automatic sequence of events which cause the instrument to periodically inject atmospheric samples into the GC column. As the sample peaks evolve from the column, the computer records their retention times for identification of the compounds and integrates their areas to determine the chemical vapor concentration in the air sample. This data is then used to update the stored information on the peak and TWA concentrations of the 10 selected contaminant gases. The entire electronics system is powered by a single, rechargeable nickel-cadmimum battery.

The expected performance of the instrument, separation of 10 contaminant gases at 1 ppm concentrations, will be achieved after some further improvement in the capillary column linings and the thermal conductivity detectors. A wide variety of chromatographic linings (stationary phases) exist today, and their adaptation and optimization in the miniature column will result in the high quality GC separations and analyses which are to be performed. Further reductions in the volume of the detector and redesign to make it removable from the column will result in the achievement of the desired 1 ppm detectivity. The miniaturization of other detectors such as the photo-ionization detector should make the instrument sensitive to contaminant vapor concentrations well below the 1 ppm level.

Development of a working prototype of the pocket-sized gas analyzer will require the utilization of silicon micromachining technology, custom integrated circuits, and hybrid packaging techniques. With the availability of these technologies, it is estimated that about 6 man-years of effort will be required to realize the first hand-held prototype of the instrument.

Realization of the pocket-size GC gas analyzer will be another example of the benefits made possible by the constructive application of silicon integrated circuits processing techniques to problems in diverse fields. The instrument will greatly expand the ability to monitor workers' exposures to toxic gases and therefore aid in the reduction of such exposures, and provide better epidemological data in future health studies. In such an application, the device should prove to be a useful analytical tool and should have significant impact on the fields of industrial hygiene and occupational safety.

APPENDIX 1

One of the classical measures of column efficiency is the plate height of the column. The plate height H relates the width of an output peak (expressed in cm) to the length of the column. For an ideal gaussian output peak with standard deviation σ_L, the plate height is given by

$$H = \frac{d\sigma_L^2}{dL} \tag{A1}$$

i.e., the increase in peak variance per unit column length. In a uniform column of length L in a constant environment, (A1) becomes

$$H = \frac{\sigma_L^2}{L} \tag{A2}$$

Expressed in terms of the volume of gas eluted from the column,

$$H = L\left(\frac{\sigma_V}{V_R'}\right)^2 \tag{A3}$$

As depicted in Figure A1, V_R' is the volume of gas eluted from the time the sample was injected to the time that the center of the peak emerged from the column. In Eq. (A3), the standard deviation σ_V is expressed in the same units as V_R'.

The number N of theoretical plates contained in a column is defined as the column length divided by the plate height,

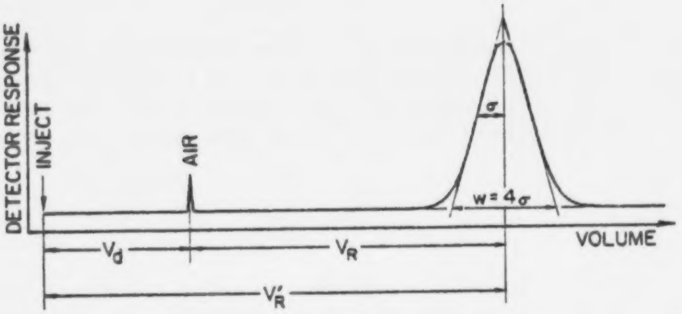
$$N = \frac{L}{H} = \left(\frac{V_R'}{\sigma_V}\right)^2 \tag{A4}$$

Instead of the standard deviation σ_V, the basewidth of the gaussian peak $w = 4\sigma_V$ is typically used in the plate equations. Therefore,

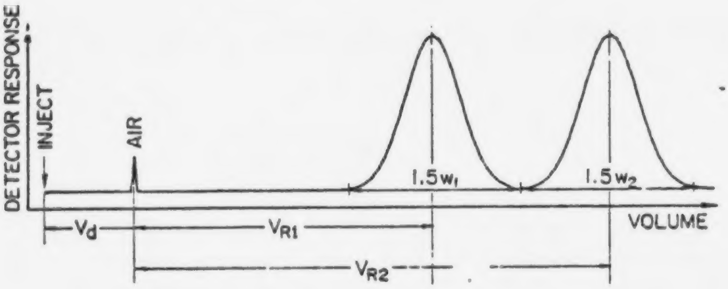
$$N = 16\left(\frac{V_R'}{w}\right)^2 \tag{A5}$$

The measured retention volume V_R' can be broken into two components, $V_R' = V_d + V_R$. V_d is the volume of gas in the column, injection, and detection systems. It is determined by the geometry of the system, and equals the retention volume of an unadsorbed gas such as air. V_R is the true retention volume of the vapor. It is the result of the retarding interaction between the sample vapor and the liquid phase.

The number of plates in the column



(a) Typical GC output.



(b) GC output -- two peaks just separated.

Figure A1. REPRESENTATION OF GC OUTPUTS DEFINING RETENTION VOLUME AND PEAK WIDTHS.

$$N = 16\left(\frac{V_d + V_R}{w}\right)^2 \qquad \text{(A6)}$$

can be viewed as a measure of column efficiency, since it relates the amount of peak distortion (spreading) to the length of time that the sample was in the column. In an efficient column, the plate height is small (1 mm or less), and the number of plates is large. What H and N do not measure, however, is the degree of separation of two sample components achieved by the column.

It has been shown [33] that as V_R is decreased by changing the amount of stationary phase in a column, the number of plates needed to just separate two sample peaks increases. However, the ratio V_R/w remains constant for all cases in which the two peaks have the same degree of separation. For this reason, a separation factor has been defined [33] as:

$$S = 16\left(\frac{V_R}{w}\right)^2 = \left(\frac{V_R}{\sigma_V}\right)^2 \qquad \text{(A7)}$$

Assuming that a gaussian peak has a width of six standard deviations (or 1.5 w), two peaks with respective retention volumes and widths V_{R1}, V_{R2}, w_1, and w_2, are just separated (as in Figure A1) when

$$V_{R2} - V_{R1} = 1.5\left(\frac{w_1 + w_2}{2}\right) \qquad \text{(A8)}$$

Assuming further that $w_1 = w_2$ (a reasonable assumption for peaks that are very close together), the separation factor is given by

$$S = 36\left(\frac{V_{R2}}{V_{R2} - V_{R1}}\right)^2 \qquad \text{(A9)}$$

Any column with that value of S, regardless of the number of plates it contains, will just separate those two vapors.

The partition ratio k is related to the retention volume of a vapor by the equation

$$k = \frac{V_R'}{V_d} \qquad \text{(A10)}$$

Using this relation and (A6) and (A7), the separation factor can be given in terms of the number of plates by

$$S = N\left(\frac{k}{1 + k}\right)^2 \qquad \text{(A11)}$$

or in terms of plate height,

$$S = \frac{L}{H}\left(\frac{k}{1 + k}\right)^2 \qquad \text{(A12)}$$

The plate height of an open-tubular capillary column with rectangular cross section has been related to the column parameters by Golay [34] as

$$H = \frac{2D_g}{u} + \left[\frac{4(1 + 9k + 51k^2/2)\, z_o^2}{105(1 + k)^2 D_g} + \frac{2k^3 z_o^2}{3(1 + k)^2 K^2 D_\ell}\right] u \qquad \text{(A13)}$$

where

z_o = 1/2 column height

u = carrier gas velocity

L = column length

k = partition ratio

D_g = diffusion coefficient of solute vapor in carrier gas

D_ℓ = diffusion coefficient of solute vapor in liquid stationary phase

K = partition coefficient

The partition ratio k used in the above equations is a function of the column height and width. It is related to a more fundamental parameter, the partition coefficient K,* by the equation

$$k = \frac{d(2z_o + Y)}{z_o Y} K \tag{A14}$$

where

d = thickness of the layer of liquid phase lining the column

Y = column width

With the substitution of (A12) and (A13), the separation factor can be expressed in terms of the column parameters,

$$S = \frac{L}{\frac{2D_g}{u}\left(\frac{k+1}{k}\right)^2 + \frac{4(1 + 9k + 51k^2/2)\, z_o^2 u}{105\, k^2 D_g} + \frac{2k z_o^2 u}{3K^2 D_\ell}} \tag{A15}$$

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*The partition coefficient is defined as the concentration of solute vapor in the stationary phase divided by the concentration in the mobile phase. It is only a function of the thermodynamic properties of the solute vapor and the stationary phase. Its exponential dependence on temperature makes it the most temperature-dependent parameter, and thus facilitates the control of the column performance with simple temperature adjustments.

GLOSSARY OF ELECTRONIC ABBREVIATIONS

A to D - analog to digital.

BCD - binary coded decimal -- individual decimal digits coded in binary notation but retaining their original decimal meaning.

CMOS - complementary metal-oxide-semiconductor -- an extremely low power integrated circuit fabrication technique which uses two types of FETs.

CPU - central processing unit -- the main numerical and control portion of a computer system.

D to A - digital to analog.

FET - field effect transistor -- a type of electronic device where an input voltage controls an output current by modifying the potentials in the semiconductor material.

FWHM - full width at half maximum -- a way of specifying the width of a gaussian peak.

hybrid - a packaging system utilizing components in chip form on an interconnecting substrate.

I/O - input/output -- the process of exchanging information between the computer and an external device.

IC - integrated circuit -- a device or process which involves the manipulation of a semiconductor on a microscopic level to obtain high density interconnected electronic devices.

JFET - junction field effect transistor -- a type of transistor with a reversed biased junction as the controlling element.

LED - light emitting diode.

LSI - large scale integration -- integrated circuits with equivalent complexity of small systems. Typically thousands of transistors on a semiconductor chip about 3 mm on a side.

monolithic - a device utilizing a single semiconductor substrate.

MOSFET - metal oxide semiconductor field effect transistor -- a type of transistor with an insulated metal electrode as the controlling element.

port - a number of input/output lines, usually used as a unit.

Tri-state - an input/output system where a line is either a high potential, a low potential, or disconnected from a data bus.

(100), (111) - designation for two of the infinite number of crystalographic planes of a semiconductor lattice.

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